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(Second Edition)

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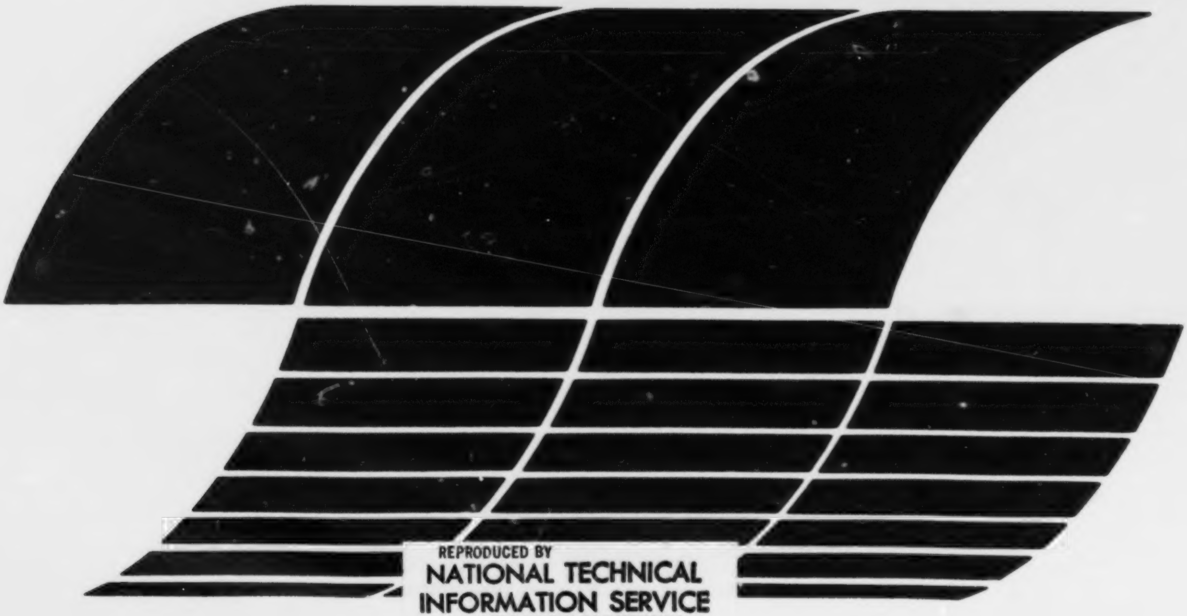

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Analyzing		
Industrial Processes	Level 1 Procedures	13H
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by

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PREFACE

The Process Measurements Branch, IERL/RTP, has developed and recommended the implementation of a three-phased sampling and analytical strategy for environmental assessment programs. The first phase, Level 1, has as its goal the class identification and semiquantitation of mass emissions within a factor of 3 for inorganic and organic compounds. The goal of Level 2 is the quantitation and identification of specific compounds present, and the goal of the third phase, Level 3, is the continuous monitoring, under various process conditions, of indicator compounds.

IERL/RTP contractors or grantees are required to use the system described in this document for environmental assessment programs in accordance with a guideline issued by IERL/RTP on April 8, 1977. It is anticipated that non-IERL-RTP organizations that are active in the environmental assessment field will also utilize this manual.

Although this guidelines manual does define Level 1 environmental assessment measurements, it is impossible to specify the exact sampling and analysis procedure for unusual circumstances. More detail and answers to specific questions may be obtained from the EPA Process Measurements Branch, IERL-RTP, Research Triangle Park. When situations arise where alternative Level 1 sampling and analysis procedures are necessary or desired, the contractor is directed to submit his alternate plan to his project officer and the Process Measurements Branch for approval before actual work is initiated.

Universal implementation of this document will result in the generation of sets of comparable data from which prioritization of the environmental insults associated with differing processes can be made.

ABSTRACT

This manual presents revised Level 1 procedures and supersedes the manual published in June 1976 (EPA-600/2-76-160a). The manual is intended for personnel experienced in collecting and analyzing samples from industrial and energy-producing processes. The phased environmental assessment strategy provides a framework for determining industrial process and stream priorities on the basis of a staged sampling and analysis technique. Level 1 is a screening phase that characterizes the pollutant potential of process influent and effluent streams.

The manual is divided into two major sections according to the procedure used. Chapters 3 through 7 discuss sampling procedures for gases, fugitive emissions, liquids (including slurries), and solids. The remainder of the manual is divided into four chapters on procedures for inorganic, organic, bioassay, and particle analyses.

LEVEL 1 PROCEDURAL MODIFICATIONS

Following is a list of changes that have been introduced into this latest edition of the Level 1 Environmental Assessment Procedures Manual.

Changes in Sampling Procedure

Item	First Edition	This Draft
SASS train passivation	50/50 nitric acid used	15% nitric acid used (pp. 67-69)
SASS filter material	Not specified	Reeve Angel 934 AH (p.67)
XAD-2 cleaning sequence	Water, methanol, ether, pentane	Water, methanol, methylene chloride (Appendix B)
SASS train	No isolation valve	Check valve in cyclone section (p.63)
SASS train leak check	0.0014 m^3/min at 508 mmHg	Front at 0.0014 m^3/min at 127 mmHg; back at 0.0014 m^3/min at 508 mmHg (p.71)
Cyclone vortex breakers	Use in all cyclones	Use only in cyclone for trapping 1- to 3-μm particles (p. 72)
Cleaning impingers	Rinse with 1:1 isopropanol/H_2O	Rinse with deionized water methanol (p. 70)
Cyclone gaskets	Teflon	Teflon or Viton A (p. 71)
Impinger solutions	750 mL each	500 mL each (p. 74)
First impinger solution	6 $\underline{M}$ H_2O_2	30% H_2O_2 (p. 74)
Fourth impinger solution	Drierite	Silica gel (p. 74)
Rinsing the back half of the SASS train	Methanol/methylene chloride	Methylene chloride (pp. 75-76)

Liquid sample volume	10 L	20-200 L (p. 93)
Gas volume (reactive gases: N and S species, organic species with bp <100° C)	Volume not specified	2 L (pp. 48-50)
Gas volume (fixed gases: O_2, N_2, CO_2, and CO)	Volume not specified	10-30 L (p. 53)
Volume of fugitive emissions particulate sample	Volume not specified	2,496 m^3 (p. 86)
Volume of fugitive vapor with or without particulate	Volume not specified	67.2 m^3 (p. 86)
Sampling device for fugitive emissions in air	Modified hi-volume sampler	FAST system or modified hi-volume sampler (pp. 84-86)

Changes in Analytical Procedure

Item	First Edition	This Edition
NO_x measurement	Single grab sample and measurement using chemiluminescence	Series of grab samples and measurement using EPA Method 7 (p. 57)
NH_3 and HCN measurement	GC using Porapak Q for 1-100 ppm detection	GC for >100 ppm (p. 54)
CO_2, CO, O_2, and N_2 measurement	GC using a single column and Molecular Sieve 5A	GC using dual columns containing Chromosorb 102 and 13X Molecular Sieve (p. 55)
SO_2 and H_2S measurement at >25 ppm	GC using Molecular Sieve 5A	GC using Porapak N (p. 55)
H_2S, SO_2, COS, CH_3SH, . . . $C_6H_{13}SH$ measurement at >1 ppb to 25 ppm	GC using 3% OV-1 Chromosorb	GC using Teflon column with 12% polyphenyl ether and 0.5% H_3PO_4 on 40/60 Chromosorb T (p. 55)

Measurement of volatile hydrocarbons	For C_1-C_6, GC using Porapak Q and isothermal	For organics bp range -160° C to +30° C, GC using Porapak Q and temperature program 60°-110° C (p. 55)
Measurement of volatile hydrocarbons	For C_7-C_{12}, GC using 1.5% OV 101 and temperature program 50° C - 150° C	For organics bp range +30° C to 100° C, GC using 20% OV 101 or Chromosorb W-HP and isothermal at 30° C (p. 56)
Measurement of nonvolatile hydrocarbons	For $>C_{13}$, use gravimetric analysis	For organics bp >100° C, measure as Total Chromatographable Organics (TCO) (pp. 140-142)
Extraction of aqueous solutions	Extract at neutral pH	Extract first at acid pH and then at alkaline pH (p. 136)
XAD-2 extraction	Use pentane	Use methylene chloride (p. 139)
Liquid chromatography (LC)	Dry packed column	Slurry packed column (p. 145)
LC	No dehydration of mixture to be separated	Dehydrate mixture to be separated using sodium sulfate at head of column (p. 145)
LC	Column temperature not controlled	Column temperature controlled (p. 144)
LC	8-fraction separation	7-fraction separation (pp. 146-148)
Infrared analysis	Use single KBr pellet to mount sample	Use double NaCl plate (preferred) or make KBr pellet to hold sample (p. 150)
Water analysis	Use Hach or similar kits for measurement of select ions	Ion chromatography preferred for measurement of these ions though Hach or similar kits still acceptable (p. 102)

Gaseous effluent opacity measurement	Ringelmann technique to be used	Previously certified observer to estimate degree of opacity (p. 81)
Detection limits for inorganic species	Specified goal of 1 ppm	Goals set according to matrix: 0.1-1 μg/m^3 for particulate matter; 0.5-10 mg/kg for noncombustible solids; 0.5-10 μg/L for liquids; and ~1 mg/m^3 for gases (1 μg/m^3 for sulfur compounds) (p. 20)
Measurement of anionic species (F^-, Cl^-, NO_2^-, NO_3^-, $SO_3^=$, $SO_4^=$, $PO_4^\equiv$, etc.)	Use wet chemical or ion-selective electrode methods	Ion chromatography is preferred though previously used methods remain acceptable (pp. 125,127,128)
Parr bomb combustion and aqua regia digestion procedures	Limited descriptions	Complete descriptions of procedures provided in appendixes (Appendix C)
Measurement of As and Sb in APS impinger solutions	Wet chemistry	Hydride evolution and atomic absorption spectrophotometry (p. 120)
Measurement of As and Sb in all other samples	Wet chemistry	Measurement along with other elements using spark source mass spectrometry (p. 115)
Instrumental resolution of the spark source mass spectrometer	Not specified	$\bar{M}/\Delta M$ specified as 3,000 (with 50% valley between peaks) (p. 115)
Quantification of SSMS data	Use the "just-disappearing-line" technique for minor components. Major components not specified.	Quantify all components of sample to 10 percent (p. 118)
Extracts of the cyclone and filter catches	Analyze for C_7-C_{12}	Not to be analyzed for TCO (p. 140)

Biological testing	General outline presented	Specific tests now summarized (pp. 167-173)
Morphological measurements	Not defined	Analysis now defined (pp. A-45, A-46)
Plan for allocation of material from SASS train for chemical and biological testing	None presented	Plan now presented (p. 80)

Miscellaneous Changes

Item	First Edition	This Edition
Pretest planning	Not discussed in detail	Discussed in moderate detail (pp. 8-14)
Quality control/quality assurance	Not discussed in detail	A chapter is dedicated to this topic (pp. 23-45)

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CHAPTER 1

INTRODUCTION

1.1 ENVIRONMENTAL ASSESSMENT PROGRAM OVERVIEW

1.1.1 Program Definition and General Goals

A sampling and analytical program has been developed for conducting environmental source assessments of the feed, product, and waste streams associated with industrial and energy processes. As described in this document and supporting references, an environmental source assessment involves: (a) a systematic evaluation of the physical, chemical, and biological characteristics of selected streams associated with a process; (b) predictions of the probable effects of those streams on the environment; (c) prioritization of those streams relative to their individual hazard potential; and (d) identification of any necessary control technology programs. An environmental source assessment program addresses, to the maximum extent possible, the identification of all potential air, water, and terrestrial pollution problems, both for pollutants for which specific standards have been set and for pollutants that are suspected to have deleterious effects on the environment and therefore may be subject to future regulation. The ultimate goal of an environmental source assessment is to insure that the materials evolving from a given processing scheme are environmentally acceptable, or that adequate control technology exists or can be developed to reduce their pollution potential.

1.1.2 Source Assessment Strategies

Two clearly distinct strategies of approach to an environmental sampling and analysis program that satisfy the requirements for producing comprehensive information are the direct approach and the phased approach. In a direct approach, all streams would be carefully sampled and the samples subjected to complete, detailed analysis for all detectable components at an overall accuracy of ±50 percent for the mass emission rates. In a phased approach, all streams would first be surveyed using simplified, generalized sampling and analytical methods that would permit their being ranked on a priority basis. Subsequent phases would then involve more extensive and detailed sampling, analysis, and long-term study of those streams determined to be of high priority. This latter or phased approach focuses available resources (both manpower and dollars) on emissions that have a high potential for causing measurable health or ecological effects, and provides comprehensive chemical and biological information on all sources of industrial emissions. Discussions of this philosophy, the information-cost benefits, and a summary of the application of the phased approach to sampling and analysis follow.

1.1.3 The Phased Approach

The phased approach, as developed by the Process Measurements Branch (PMB) of the Environmental Protection Agency, requires three separate levels of sampling and analytical effort. The first level, Level 1, utilizes quantitative sampling and analysis procedures that yield final analytical results accurate to within a factor of 3 of the sample. (See Section 1.2.3 for more discussion of this error limit.) Level 1 is designed to (a) provide preliminary environmental assessment data, (b) identify problem areas, and (c) formulate the data needed for the prioritization of energy and industrial processes, streams within a process, components within a stream, and classes of materials for further consideration in the overall assessment. The second sampling and analysis effort, Level 2, is directed by Level 1 results and is designed to provide additional information that will confirm and expand the information gathered in Level 1. This information will be used to define control technology needs, and may, in some cases, give the probable or exact cause of a given problem. The third phase, Level 3, involves monitoring the specific problems identified in Level 2 so that the critical components in a stream can be determined exactly as a function of time and process variation for control device development.

The three sampling and analysis levels are closely linked in the overall environmental assessment effort. Level 1 identifies the questions that must be answered by Level 2, and Level 3 monitors the problems identified in

Level 2 to provide information for control device design and development. For example, if a Level 1 test indicated that polycyclic organic material (POM) might be present in significant amounts and also gave a positive mutagenicity test, Level 2 sampling and analysis would be designed to determine the exact quantities of organic constituents, the percentage of POM, and the identity of as many specific POM compounds present as is economically possible. In addition, using the Level 1 data and any available Level 2 results, the sample would be retested for cytotoxicity and mutagenicity in order to confirm and expand the total bioassay information. A test for carcinogenicity would also be run if the results of these tests were positive.

The phased approach offers potential benefits in terms of the quality of information that is obtained for a given level of effort and in terms of the costs per unit of information. This approach has been investigated and compared to the more traditional approaches (ref. 1) and has been found to offer the possibility of substantial savings in both time and funds required for assessment.

1.2 LEVEL 1 OVERVIEW

1.2.1 Level 1 in a Phased Approach

The Level 1 sampling and analysis program is designed to produce a comprehensive survey of emissions from any industry or energy-generating facility that might be of environmental consequence. This survey shows, within broad general limits, the absence or presence, the approximate concentrations, and the emission rates of inorganic elements, selected anions, and classes of organic compounds in gaseous, liquid, and solid samples. Any particulate matter suspended in the effluent gases is analyzed separately for chemical composition, for size, and for other physical parameters that can be determined by microscopic examination. Selective biotesting is performed on samples to obtain information indicative of the possible human health and ecological effects of the material. If it can be proven that equivalent Level 1 data exist for all streams of interest, then a Level 1 effort need not be conducted. If only partial data exist, then a complete complement of Level 1 tests must be performed on all streams.

The Level 1 methods of sampling and analysis are chosen on the basis of their information outputs, their cost effectiveness, their availability, their reliability, and their ease of application. Whenever possible, standard EPA-recognized methods are employed; however, due to the comprehensive nature of the information requirements of Level 1 assessment, new and sometimes developmental methods are used to fill these needs. The efforts of competent samplers, biologists, microscopists, engineers, analytical inorganic chemists, and organic chemists will be required to produce quality information from these environmental assessment endeavors.

It is anticipated that many process streams tested by these techniques will contain only nonhazardous substances, or hazardous substances in nonhazardous concentrations. This would mean that more extensive testing of the source and application of additional control devices would be unwarranted at this time. When Level 1 results identify possible hazardous emissions, those specific streams will be priority-ranked and scheduled for the intensive investigation of Level 2 efforts. Level 1 findings will continue to provide useful information in Level 2 tests by the delineation of specific sampling, analysis, and decisionmaking problem areas. These outputs also help direct subsequent planning and the preliminary choice of methodology for the Level 2 effort so that the additional information needs will be satisfied effectively.

1.2.2 Level 1 Analytical Scheme

As indicated above, the Level 1 philosophy involves a multimedia approach. Solids and liquids are to be analyzed according to the scheme shown in Figure 1. Flue gases and particulates are to be collected by means of a Source Assessment Sampling System (SASS) train (see Chapter 4) and are to be analyzed according to the scheme shown in Figure 2. The techniques to be used in the analysis scheme are listed in Table 1.

1.2.3 Level 1 Quantitative Goals

The goal of Level 1 assessment is to identify the pollution potential of a source in a quantitative manner, with a target accuracy factor of 3. That is, the final analytical result obtained should be between 1/3 and 3 times the "true" value. Those familiar with environmental problems will

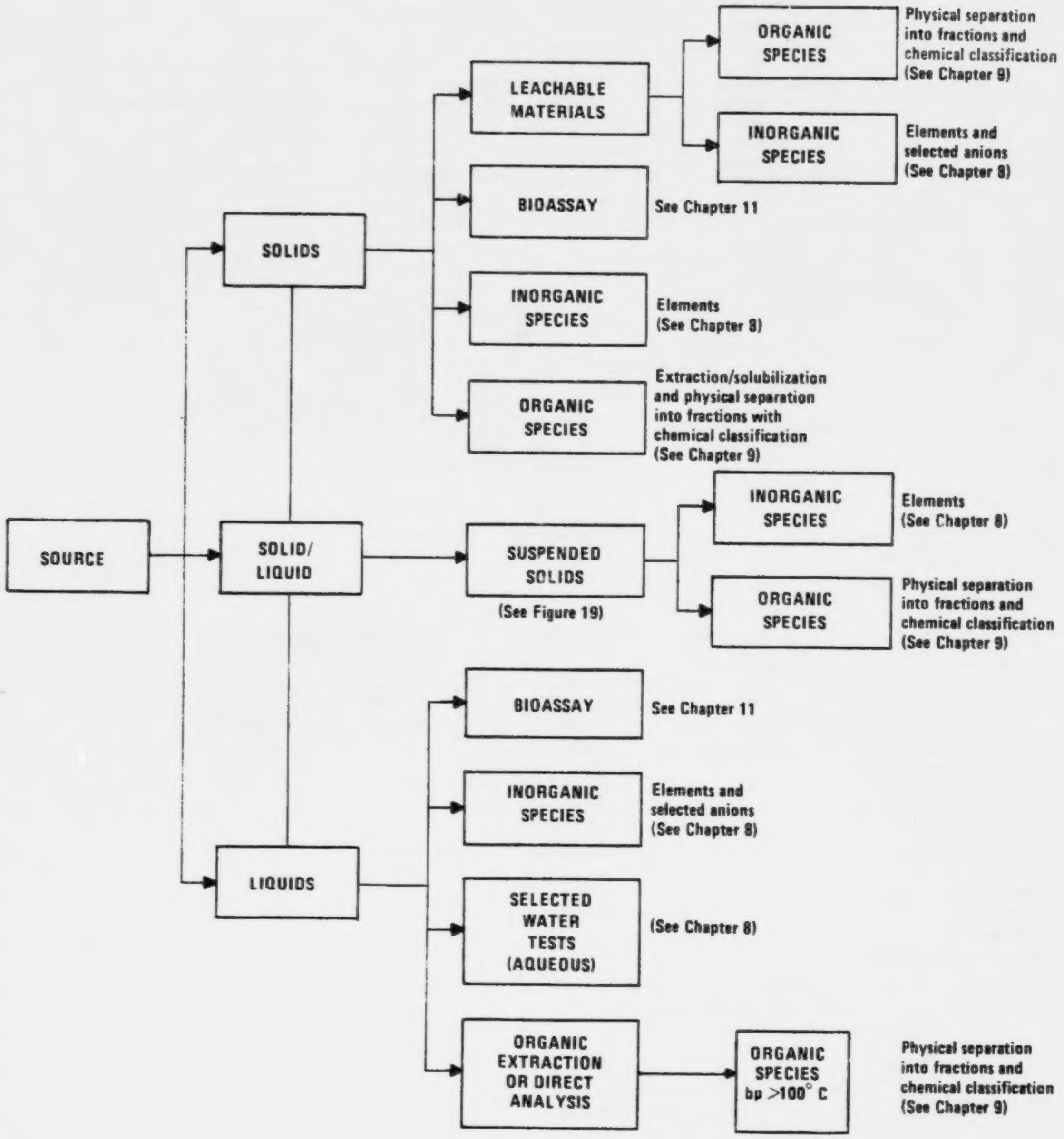
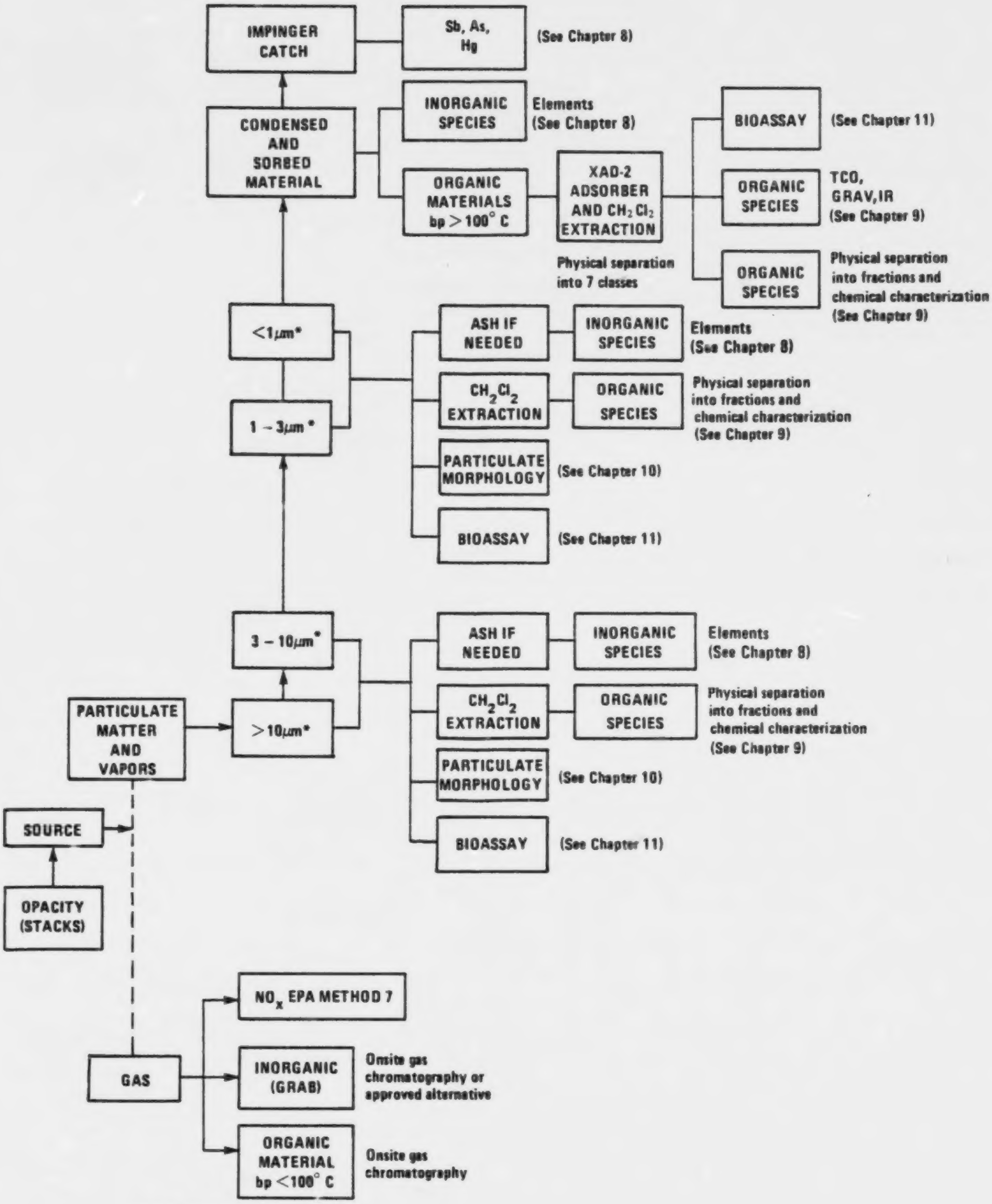

SOURCE
SOLIDS
SOLID/ LIQUID
LIQUIDS
LEACHABLE MATERIALS
ORGANIC SPECIES
Physical separation into fractions and chemical classification (See Chapter 9)
INORGANIC SPECIES
Elements and selected anions (See Chapter 8)
BIOASSAY
See Chapter 11
INORGANIC SPECIES
Elements (See Chapter 8)
ORGANIC SPECIES
Extraction/solubilization and physical separation into fractions with chemical classification (See Chapter 9)
SUSPENDED SOLIDS
(See Figure 19)
INORGANIC SPECIES
Elements (See Chapter 8)
ORGANIC SPECIES
Physical separation into fractions and chemical classification (See Chapter 9)
BIOASSAY
See Chapter 11
INORGANIC SPECIES
Elements and selected anions (See Chapter 8)
SELECTED WATER TESTS (AQUEOUS)
(See Chapter 8)
ORGANIC EXTRACTION OR DIRECT ANALYSIS
ORGANIC SPECIES bp >100° C
Physical separation into fractions and chemical classification (See Chapter 9)

Figure 1. Basic Level 1 sampling and analytical scheme for solids, slurries, and liquids.


IMPINGER CATCH
Sb, As, Hg
(See Chapter 8)
CONDENSED AND SORBED MATERIAL
INORGANIC SPECIES
Elements (See Chapter 8)
ORGANIC MATERIALS bp > 100° C
XAD-2 ADSORBER AND CH2Cl2 EXTRACTION
Physical separation into 7 classes
BIOASSAY
(See Chapter 11)
ORGANIC SPECIES
TCO, GRAV, IR (See Chapter 9)
ORGANIC SPECIES
Physical separation into fractions and chemical characterization (See Chapter 9)
<1μm*
1 – 3μm*
ASH IF NEEDED
INORGANIC SPECIES
Elements (See Chapter 8)
CH2Cl2 EXTRACTION
ORGANIC SPECIES
Physical separation into fractions and chemical characterization (See Chapter 9)
PARTICULATE MORPHOLOGY
(See Chapter 10)
BIOASSAY
(See Chapter 11)
3 – 10μm*
>10μm*
PARTICULATE MATTER AND VAPORS
ASH IF NEEDED
INORGANIC SPECIES
Elements (See Chapter 8)
CH2Cl2 EXTRACTION
ORGANIC SPECIES
Physical separation into fractions and chemical characterization (See Chapter 9)
PARTICULATE MORPHOLOGY
(See Chapter 10)
BIOASSAY
(See Chapter 11)
SOURCE
OPACITY (STACKS)
NOx EPA METHOD 7
GAS
INORGANIC (GRAB)
Onsite gas chromatography or approved alternative
ORGANIC MATERIAL bp < 100° C
Onsite gas chromatography

*WEIGH INDIVIDUAL CATCHES

Figure 2. Basic Level 1 sampling and analytical scheme for particulates and gases.

TABLE 1. BASIC LEVEL 1 ANALYSES

Physical:	Cyclone particle size
	Optical microscopy
Chemical:	Spark source mass spectrometry (SSMS)
	Atomic absorption spectroscopy (AAS)
	Wet chemical (selected anions)
	Gas chromatography (GC)
	Elution chromatography (LC)
	Ion chromatography (IC)
	Infrared spectrometry (IR)
	Low resolution mass spectrometry (LRMS)
	Total chromatographable organic (TCO)
Biological:	Rodent acute toxicity
	Microbial mutagenesis
	Cytotoxicity
	Fish acute toxicity
	Algal bioassay
	Soil microcosm
	Plant stress ethylene

recognize that this accuracy factor is not as liberal as it might seem. Real sample procurement problems and matrix effects may contribute unknown errors to an overall analytical scheme that utilizes quite accurate measurement techniques (AAS, for example). To minimize the effects of these possible difficulties, care must be exercised in each step of the Level 1 procedures. This is well-demonstrated by the variance relationship between the standard deviations (s) for a total procedure and the parts of that procedure. That is, for a typical procedure,

$$s_{\text{total}} = \left[s^2_{\text{sampling}} + s^2_{\substack{\text{sample}\\ \text{treatment}}} + s^2_{\text{measurement}} \right]^{\frac{1}{2}}.$$

If each step has a relative standard deviation of ±20 percent, the total relative standard deviation would be approximately ±35 percent. Allowing each step to have a relative standard deviation of ±50 percent would lead to a s_{total} of ±87 percent, which is beyond the -70 percent (1/3 of true value) goal of the Level 1 program. Again, reasonable care must be exercised in all of the Level 1 sampling and analytical techniques.

1.3 LEVEL 1 ASSESSMENT PROTOCOL

Level 1 assessment can be divided into the following formal steps: Pretest Planning, Pretest Site Survey, Sampling, and Analysis. Each is important to the performance of a high-quality assessment.

1.3.1. Pretest Planning

The final decision to test a particular plant will be the result of the prioritization studies and of the preliminary selection process based on the site selection criteria of a given program and on the data requirements of the overall program or general EPA objective.

Before the actual sampling and analysis effort is initiated, the data requirements must be established and used to help identify test requirements as well as any anticipated problems. The following paragraphs present a general summary of these requirements and planning functions; they must be applied or expanded to meet the needs of the individual tests to be performed. Specific recommendations concerning data requirements associated with each of the process streams are discussed in the appropriate chapters of this manual.

Before traveling to a plant for a pretest site survey, it is necessary to become familiar with the processes used at the site. This involves understanding the chemistry and operational characteristics of the various unit operations as well as any pollution control devices or processes. It is particularly important to know that detailed relevant process data are necessary for the sampling and analysis effort as well as for the overall environmental assessment for the following reasons.

a. From a knowledge of the process and the composition of input materials and products, conclusions about pollutants likely to be found in waste streams can be drawn. This should not, however, result in the deletion of portions of Level 1 activities.

b. One must know where to look for waste streams, including fugitive emissions.

c. One must know how plant operating conditions are likely to affect waste stream flow rates and compositions.

d. Thorough familiarity with the process permits design of proper sampling programs.

e. Thorough knowledge of the interrelationships among process variables permits extrapolation to conditions in other systems (larger or smaller) being assessed.

f. Detailed process data are the basis from which control technology development programs proceed, should environmental assessments indicate such need.

Familiarization with the process is also necessary so that a checklist of the requisite data can be developed, including temperatures, pressures, flow rates, and variations of conditions with time for the pretest site survey.

For any given sampling and analysis task, the data collected must be consistent with the overall Level 1 objectives. Thus, the minimum amount of data for a given stream is flow rate per unit time at a given temperature and pressure. It is expected that professional sampling and analysis personnel, in conjunction with the EPA Project Officer and the Process Measurements Branch, Industrial Environmental Research Laboratory (PMB-IERL), will select the appropriate data requirements for a given industry.

1.3.2 Pretest Site Survey (ref. 2)

1.3.2.1 General--

After establishing the necessary process data needs and selecting a tentative set of sampling points, a pretest site survey should be performed. At the test site, the survey team should meet with the plant engineer to verify the accuracy of the existing information and arrange for the addition of any missing data. Using this information and detailed, accurate process flow diagrams, the survey team will then proceed to select the actual sampling sites with the following criteria in mind:

a. The sampling points should provide an adequate base of data for characterizing the effluent stream of the source within a factor of 3.

b. When possible, each sampling point should provide a representative sample of the effluent streams.

c. The sampling site must have a reasonably favorable working environment. The survey personnel must consider what the temperature and noise levels are in the sampling areas, if protection from rain or strong winds exists, and whether scaffolding, ladders, pulleys, etc., are safe.

The identification of support facilities and services is an essential aspect of the site survey. In an effort to minimize the requests made upon the operators and to minimize scheduling problems for these support services, it is desirable that the onsite laboratory operate completely independently of external support facilities.

The results of the pretest site survey must be sufficiently detailed so that the field test problem of sampling the correct process stream at the proper sampling location and using the appropriate methodology will be completely defined prior to arrival of the field test team at the source site.

1.3.2.2 Sampling for Gaseous Components--

A pretest Level 1 site survey of process streams and vents involves the following steps:

a. Tracing the process flow to establish gaseous outputs. Using the process flow diagrams as a guide, a physical inspection of the system must be conducted to uncover any undocumented output sources or unrecorded equipment modifications.

b. Locating and itemizing process vents.

c. Locating and itemizing stacks and flares.

d. Recording the physical parameters of the stream in as much detail as possible.

Aside from these general considerations, there are two specific requirements for gas and vapor sampling:

a. All process streams and vent systems recirculated into process streams will require in-line valves for sampling.

b. All vents to the atmosphere require a means of access as well as suitable working space for personnel involved in the sampling process.

1.3.2.3 Sampling for Particulates--

In performing the pretest site survey, the crew should provide for the following requirements of the Source Assessment Sampling System:

a. The sampling port: To accommodate the sampling probe, the port must have an opening of at least 2-1/2 in. A 3-in. nipple welded to the stack is usually the best way to obtain access. The port must be centered and at least 13 in. above the platform to comply with the oven clearance requirements.

b. The test platform: The size of the test platform, which supports the sampling equipment and test personnel, depends on the length of the probe to be used. For the standard 5-ft probe, an ideal platform would be 13 ft long and 8 ft wide. If such large platforms are not available, compromises must be made prior to sampling.

c. Electrical power: Power is required for the probe and oven heaters, for the organic sorbent module water circulation pump, and for the two vacuum pumps. To operate the entire system, a total of two 30-A circuits or four 15-A circuits are required.

d. Ice for cooling the impinger train: A source of large quantities of ice should be located near the sampling location. At normal temperatures (205° C at the oven and 20° C at the sorbent cartridge inlet), 15 to 50 lb of ice will be required per hour of testing.

1.3.2.4 Fugitive Emissions--

Fugitive emission sampling will be performed whenever there is a likelihood of there being a significant amount of this material generated at a given site. Planning Level 1 fugitive emissions sampling requires knowledge of the probable sources of emissions, the processes and materials involved, the operating schedules of sources and processes, the physical arrangement of the site, and general meteorological and topographical characteristics. Most of the required information can be gathered during the pretest survey of the site: the physical aspects through personal observation, and the remaining aspects from historical data provided by the site operators and local weather stations.

In performing a pretest site survey, the program planner should obtain the following information:

a. Site description: A general plan of the site with sufficient detail to indicate the processes of concern, the location of emission sources, important topographical features, etc.

b. Prevailing wind data: Typically, a local wind rose to indicate the most probable wind direction and speed ranges.

c. Fugitive emissions sources: A physical description of the sources to be measured, the processes involved, and their location in the site plan.

d. Fugitive emissions to be measured: Classification as particulates, gases, etc.; categorization per definitions; estimations of magnitude (cloud or plume size and distribution); concentration (visibility of cloud or plume); and frequency (continuous or cyclic).

e. Sampler requirements: Number and type of samplers.

f. Sampler locations: Approximate for prevalent and alternative conditions.

g. Sampling schedule: Approximate number and duration of samplings to be performed.

Sampler locations can only be suggested in the planning of the assessment program since it is impossible to predict what meteorological and process conditions will exist during the actual assessment. A good plan will suggest primary sampler locations based on the most likely conditions and alternate locations for secondary conditions.

1.3.2.5 Liquid and Slurry Sampling--

The same criteria for locating a gas sampling point can be applied to locating sampling sites for liquid samples. A review of those criteria and procedures is contained in Section 1.3.2.1 of this chapter.

While the site selection criteria for gas and liquid sampling are generally the same, the test personnel must be aware of the problems associated with the sampling of liquids and how these factors affect the choice of a sampling site. Two factors will affect the selection of a sampling site for liquid/slurry streams:

a. Stream homogeneity: This is the most important problem that must be addressed by the site survey crew. Unlike gas streams, which mix fairly evenly, liquid streams tend to be more stratified because of lower thermal agitation and higher fluid viscosities.
b. Stream flow rate: Large, slow-moving streams will offer more of a chance for stratification to occur. This factor is especially important in large pipes or open sluices and ditches.

1.3.2.6 Solid Sampling--

Solid input and output streams in most process operations consist of fuels, primary reaction components, treatment or maintenance chemicals, and marketable output products or output refuse products. These solids range from very fine powders to very coarse lumps. This variation in sample consistency influences the sampling technique to be used, which must be established in the pretest site survey. For the purpose of the pretest site survey, therefore, the following questions must be answered:

a. Can the material be sampled as it enters or leaves the process, or must it be sampled in its storage or pile form?
b. If the material can be sampled as it enters or leaves the process, what is the nature of the conveyor system (belt, worm screw, duct) and what is the closest available sampling location to process entry and farthest available sampling location from process exit?
c. What is the consistency of the material (powder, coarse grain, lump) and what is the apparent variance within this consistency?
d. What is the approximate size of the storage reserve and what is the method of access to said reserve?

1.3.2.7 Pretest Site Survey Forms--

The information to be obtained during a pretest site survey has been discussed in detail. To assist the reader in developing an overview of this survey, copies of pretest site survey forms to be used on an actual survey are included in Appendix A of this manual.

1.3.3 Sampling

Level 1 sampling stresses the concept of completeness by presuming that any and all streams leaving the process will be sampled unless data equivalent to Level 1 programmatic output already exist. Further, Level 1 sampling is not predicated on a priori judgments as to stream composition. The techniques utilized presume that whatever a priori knowledge is available is, at best, incomplete. Predictive and extrapolative techniques employed during source assessments serve as a check on the empirical data and not as a replacement for them. Level 1 sampling systems are therefore designed to permit collection of all substances in the stream at a reasonably high level of efficiency. They do not necessarily produce information as to specific substances or their chemical form. Further, Level 1 sampling programs are designed to make maximum use of existing stream access sites. While care must be exercised to insure that the samples are not biased, the commonly applied concepts of multiple point, isokinetic, or flow proportional sampling are not rigidly adhered to.

The Level 1 procedures described in this manual can be utilized to acquire process samples, effluent samples, and feed stock samples. The Level 1 environmental assessment program must, at a minimum, acquire a sample from each process feed stock stream and from each process effluent stream. Samples of fugitive air/water emissions are obtained only when circumstances indicate the need. The data obtained from the feed streams are necessary to establish a baseline for comparison. The effluent stream sampling program is required to estimate the mass emissions rate and the environmental impact that will result. Sampling and analytical procedures that are required to support a comprehensive environmental source assessment must be multimedia in nature.

1.3.3.1 Classification of Streams for Sampling Purposes--

The basic multimedia sampling strategy (shown in overview form in Figure 3) has been organized around the five general types of sampling found in industrial and energy-producing processes rather than around the analytical procedures that are required on the collected samples. This facilitates the complex and difficult task of organizing the manpower and equipment necessary for successful field sampling and establishing meaningful units of cost.

The five sample types are:

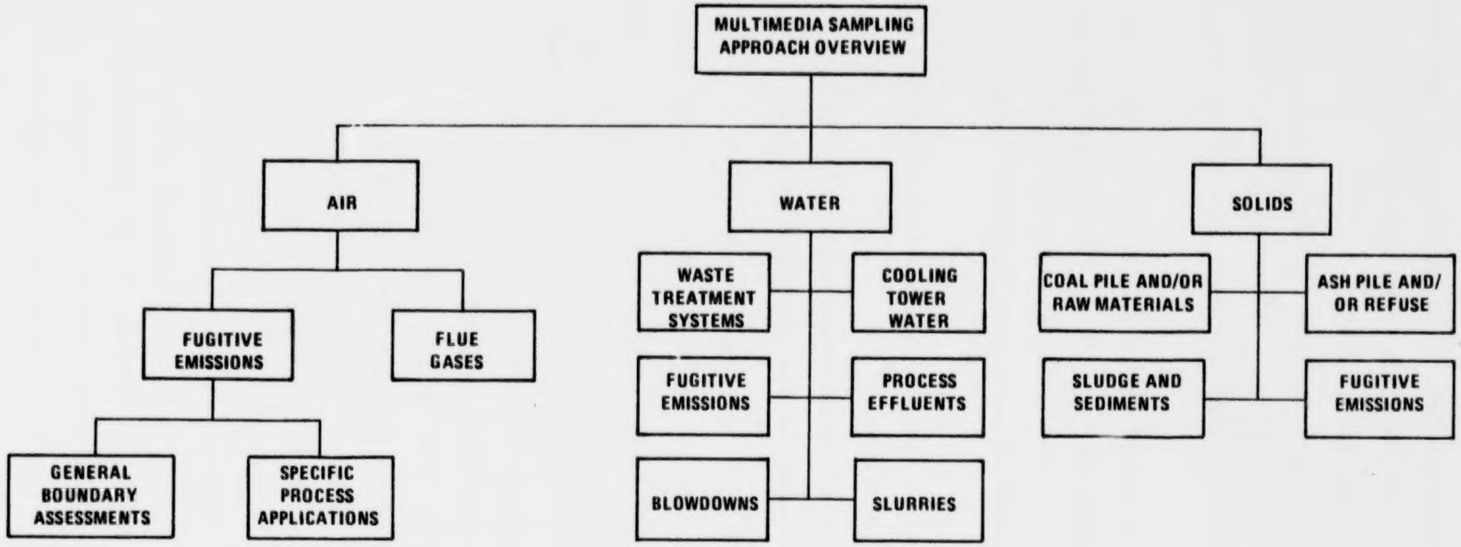

MULTIMEDIA SAMPLING APPROACH OVERVIEW
AIR
FUGITIVE EMISSIONS
FLUE GASES
GENERAL BOUNDARY ASSESSMENTS
SPECIFIC PROCESS APPLICATIONS
WATER
WASTE TREATMENT SYSTEMS
COOLING TOWER WATER
FUGITIVE EMISSIONS
PROCESS EFFLUENTS
BLOWDOWNS
SLURRIES
SOLIDS
COAL PILE AND/OR RAW MATERIALS
ASH PILE AND/ OR REFUSE
SLUDGE AND SEDIMENTS
FUGITIVE EMISSIONS

Figure 3. Multimedia sampling strategy overview.

a. Gas/vapor: These are samples for light hydrocarbon and inorganic gas analysis. They include samples from input and output process streams, process vents, and ambient air.

b. Liquid/slurry streams: Liquid streams are defined as those containing less than 5 percent solids. Slurries are defined as those containing greater than 5 percent solids. Nonflowing pastes are considered solids.

c. Solids: These include a broad range of material sizes from large lumps to powders and dusts as well as nonflowing wet pastes. Because the distinction between solids and slurries can become blurred, the reader should consult both Chapters 6 and 7 of this manual when in doubt.

d. Particulates or aerosols: These emissions are found in contained streams such as ducts or stacks.

e. Fugitive emissions: These are gaseous and/or particulate emissions from the overall plant or various process units.

1.3.3.2 Phased Approach Sampling Point Selection Criteria--

The selection of sampling points in processes where phased-level sampling techniques are employed is based on the concept previously stated: that Level 1 sampling is oriented toward obtaining quantitative data with relaxed accuracy requirements for determination of the pollution potential of a source, whereas Level 2 sampling is intended to acquire the more accurate data necessary for a definitive environmental assessment on prioritized streams. Stream parameters such as flow rates, temperature, pressure, and other physical characteristics will be obtained on both levels within the accuracy requirements of a given level of sampling. For example, a Level 1 particulate matter sample is obtained at a single point under pseudoisokinetic conditions. This means that the sample is acquired at the point of average velocity, which has been determined by a velocity traverse taken at typical points in the stream. The sample is withdrawn at an appropriate rate through the SASS train cyclones (see Chapter 4) by using a probe nozzle that is specifically selected for isokinetic conditions; however, this flow rate must not be allowed to change since a change in flow rate will alter the particle cutoff efficiency of the cyclone system. In Level 2, however, where quantitative data requirements may be more stringent, isokinetic samples must be withdrawn using a full traverse with a port in specific locations away from ducting bends and other obstructions in order to insure a sample representative of the actual effluent. The recommendations in this manual are restricted to Level 1 sampling and analysis criteria only.

Similar considerations apply to site selection for sampling liquids and solids. In Level 1, liquid samples can be taken from tanks or other containers without extensive depth integration using a multiported probe. Pipes may be accessed with a simple tap sampler. In slurry streams, an effort should be made to sample a turbulent or well-mixed area.

In the case of solids sampling, the standard procedures used in sampling piles and stationary containers are relaxed on Level 1 both by taking fewer increments to make a composite and by relaxing the requirements for depth-integrated sampling. For moving solid streams, a simplified sample is obtained by reducing the number of increments required for the time-averaging aspect of the sampling procedure.

In most cases, Level 1 sampling methods generally encompass approved standard EPA, American Society for Testing and Materials (ASTM), and American Petroleum Institute (API) techniques. Modifications are then made to these techniques to adapt them to the time and cost constraints consistent with the Level 1 sampling philosophy. These modifications include: (a) reducing port selection criteria; (b) eliminating the requirements for traversing, continuous isokinetic sampling, and replicate sampling in the collection of particulate matter; and (c) use of grab samples for some gaseous, liquid, and solid samples.

1.3.3.3 Sampling Requirements--

Guidelines indicating amounts of sample to be collected in order to carry out meaningful analyses have been developed. These amounts are presented in Table 2. Further details regarding sampling are provided in later chapters of this manual.

TABLE 2. REQUIREMENTS FOR LEVEL 1 STREAM SAMPLING

Stream	Sample size	Location	Sample procedure
Vapors with or without particulate	30 m^3	Ducts, stacks	SASS train
Liquid	20 L*	Lines or tanks	Tap or valve sampling
		Open free-flowing streams	Dipper method or composite sampler
Solids	1 kg	Storage piles	Coring
		Conveyors	Full stream cut
Gas (reactive) organic material with bp <100° C; N and S species	2 L	Ducts, stacks, pipelines, vents	Grab sample (glass bulb)
Gas (fixed) O_2, N_2, CO_2, and CO	10-30 L	Ducts, stacks, pipelines, vents	Integrated bag sample
Fugitive emission	2,496 m^3	Ambient atmosphere	FAST or modified hi-vol

*May need additional sample volume depending on the nature of the biotesting employed.

1.3.4 Level 1 Analysis

During an environmental source assessment, the analytical methods applied will vary from relatively simple manual wet chemistry to relatively complex instrumental techniques. Analyses proceed from general, broadly applicable survey methods to more specialized techniques tailored to specific component measurements. This broad range requirement has been structured to adhere to the same phased concept described for the sampling program. At each level of the analytical program, the depth and sophistication of the techniques are designed to be commensurate with the quality of the samples taken and the information required. Hence, expenditure of analytical resources on screening samples from streams of unknown pollution potential is minimized.

1.3.4.1 Analytical Methodologies--

Chapters 8 through 11 specify analysis schemes and procedures that will provide data relatable to all existing EPA standards and those additional data requirements specified above for Level 1 environmental assessment.

There are seven categories of analysis:

a. Organic analysis: Survey techniques are used to identify compound classes by functional group.
b. Inorganic element analysis: Based on spark source mass spectroscopy (SSMS), which can perform a general survey of all effluent streams for possible inorganic elements. Atomic absorption spectrophotometry is to be used for analysis of mercury. Antimony and arsenic quantitations will also be made using atomic absorption spectrophotometry on the impinger solutions.
c. Particulate morphology: Includes microscopic examination of shape, size distribution, surface features, for possible source assignment.
d. Water analysis: Ion chromatography and reagent test kits will be used as a supplement for those analyses not covered by SSMS or organic analysis.
e. Gas chromatographic analysis: Consists of onsite analysis of gaseous and/or low boiling organic and inorganic species.
f. Opacity: Consists of onsite evaluation of smoke plume light transmittance.
g. Bioassay testing: Includes selected health and ecological testing on all solid and liquid samples, and is designed to measure the environmental and health effects potential of a given source stream in a broad and general manner.

The three major categories, though, are organic analysis, inorganic analysis, and bioassay testing.

The Level 1 organic analysis achieves a semiquantitative estimate of the predominant classes of organic compounds present in samples taken from process streams. The Level 1 strategy is to isolate well-defined fractions by conventional liquid chromatography rather than to isolate specific classes.

Level 1 inorganic analysis utilizes the spark source mass spectroscopic technique to achieve qualitative and semiquantitative elemental analyses on all solids, particulates, filterable solids from liquid streams, and evaporated residues of liquid samples. This technique is used because of its general multielement capability, acceptable detection limits, speed, and cost. Atomic absorption spectrometry is to be used for those elements and/or samples for which SSMS is not suitable or appropriate; for example, mercury. An overview of the scheme for analysis of organic and inorganic species is presented in Figure 4.

Biological tests included in the Level 1 analysis scheme are intended to indicate potential biohazards independently of chemical analysis. While chemical analysis provides quantitation for known dangerous compounds, bioassay provides complementary information on the unclassified compounds and their mixtures. The biological test matrix presently being applied allows for the individual design of testing employed relative to a particular sample. Only the appropriate tests are selected from the representative health and environmental effects indicators.

1.3.4.2 Level 1 Detection Limit--

On the basis of environmental concern and/or potential health effects, the nature of the analytical techniques to be used, and the amount of sample that can be practically collected, acceptable and attainable detection limits have been identified. These attainable detection limits for inorganic species will vary with the element and the sample matrix but should be within the limits of 0.002-0.2 $\mu g/m^3$ with particulate matter, 0.02-2 mg/kg with noncombustible solids, 0.2-2 $\mu g/L$ with liquids and ~1 mg/m^3 with gases (1 $\mu g/m^3$ for sulfur compounds). See Section 8.3.4 and Table 14 for further discussion.

A realistic detection limit of the TCO organic analysis procedure with environmental assessment samples is 100 ng/injected sample while that of the gravimetric analysis is 1 mg/column aliquot. The resultant sample detection limits will be variable according to the concentration factor applicable to that particular analysis. See Section 9.4.4.4 for further details.

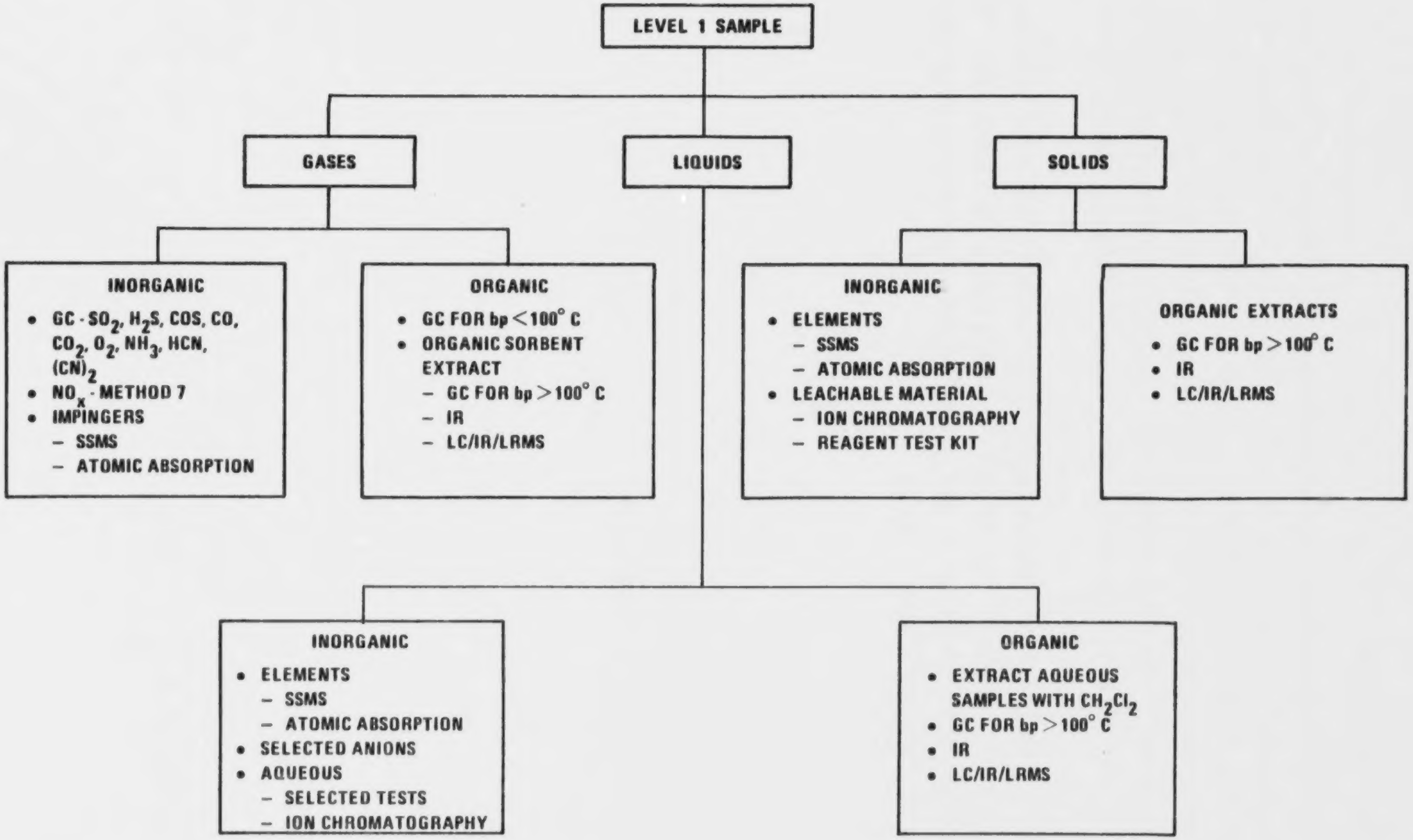

LEVEL 1 SAMPLE
GASES
LIQUIDS
SOLIDS
INORGANIC
• GC - SO_2, H_2S, COS, CO, CO_2, O_2, NH_3, HCN, $(CN)_2$
• NO_x - METHOD 7
• IMPINGERS
– SSMS
– ATOMIC ABSORPTION
ORGANIC
• GC FOR bp < 100° C
• ORGANIC SORBENT EXTRACT
– GC FOR bp > 100° C
– IR
– LC/IR/LRMS
INORGANIC
• ELEMENTS
– SSMS
– ATOMIC ABSORPTION
• LEACHABLE MATERIAL
– ION CHROMATOGRAPHY
– REAGENT TEST KIT
ORGANIC EXTRACTS
• GC FOR bp > 100° C
• IR
• LC/IR/LRMS
INORGANIC
• ELEMENTS
– SSMS
– ATOMIC ABSORPTION
• SELECTED ANIONS
• AQUEOUS
– SELECTED TESTS
– ION CHROMATOGRAPHY
ORGANIC
• EXTRACT AQUEOUS SAMPLES WITH CH_2Cl_2
• GC FOR bp > 100° C
• IR
• LC/IR/LRMS

Figure 4. Multimedia analysis overview.

1.4 SUMMARY AND CONCLUSIONS

The three-phased approach to source assessment is reasonable from both scientific and economic points of view. The first phase of this three-phased program is designed to be comprehensive in terms of detection of all effluents above some minimum levels, though exacting quantification is not required. Nevertheless, this first phase, Level 1, will provide useful information and give direction to the second sampling and analysis effort, Level 2.

The following chapters provide detailed information about the various aspects of the Level 1 program including multimedia sampling techniques, the analytical methodologies to be used, and guidelines for quality control and quality assurance throughout the program.

CHAPTER 2

QUALITY CONTROL/QUALITY ASSURANCE*

2.1 INTRODUCTION

As discussed in Chapter 1, the goal of the Level 1 program is to acquire environmental assessment data having an accuracy factor of 3. Since virtually nothing is known _a priori_ about the composition of a given sample, the analyst cannot count on being able to recognize a spurious result or artifact except by comparison with concurrently analyzed controls. Furthermore, the analyst is not able to predict, on the basis of past experience, what precautions are necessary and sufficient to maintain the integrity of the (unknown) sample components. Finally, because Level 1 environmental assessment (EA) samples are not taken in duplicate and because in most instances the sample cannot be split into aliquots without changing the effective limits of detection, the analyst has, basically, only one opportunity to treat each sample correctly.

Conventional statistical parameters are based on the concepts of replicate analyses (precision) and independently verified true values (accuracy). Since each Level 1 EA sample is unique and presumed to be totally unknown, these concepts do not rigorously apply to the EA samples themselves. Calibration standards can and will be used in all analyses. It can be assumed that values obtained for samples are no better, in terms of precision and accuracy, than those obtained for standards; they may be considerably worse if the sample matrix introduces substantial interferences.

Given these Level 1 objectives and constraints, and given also the fact that the Level 1 sampling procedures are not designed to provide a rigorously representative sample in all cases, it is clearly not cost-effective to concentrate a large amount of resources to attempt to achieve very high precision in the analytical laboratory. It is suggested, therefore, that the analyst aim for a precision, expressed as a coefficient of variation (relative standard deviation), for within-laboratory analyses of about 10 percent in each quantitative operation involved in Level 1 analyses. Thus, calibration data should be rejected if replicate determinations on standards indicate that the precision criterion is not being satisfied. Similarly, the phrase "quantitatively transfer" should be taken to mean that at least 90 percent of the sample is transferred. Although the 10 percent guideline may not be rigorously related to the overall "factor of 3" criterion, it would seem to provide the analyst with a working criterion that is consistent with the objectives of the Level 1 environmental assessment.

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*For a more detailed discussion see _Guidelines for Environmental Assessment Data Quality Programs_ (ref. 3).

A program of suitable laboratory techniques (SLT), quality control (QC), and quality assurance (QA) is necessary to assure that this desired accuracy goal is attained. In the area of chemical analysis, the analyst is responsible for putting into effect both good laboratory practices and quality control. This is different from an industrial situation where, for example, one group is involved in manufacture and another in quality control. With this difference in mind, this chapter has been divided into three parts. Good laboratory practices and some quality control procedures will be discussed first, followed by a discussion of quality control and then a discussion of quality assurance.

2.2 SUITABLE LABORATORY TECHNIQUES

A program of suitable laboratory techniques can be divided into the following areas of concern:

a. Material and equipment procurement,
b. Cleanliness,
c. Metrology and standardization,
d. Sampling,
e. Analysis procedures, and
f. Data computation and reporting.

2.2.1 Material and Equipment Procurement Controls

In the Level 1 program, this factor would relate to sampling apparatus, analytical instrumentation, and chemical reagents. Sampling apparatus, whether purchased or constructed in-house, should be constructed of corrosion-resistant materials, should be designed to be safe to use and relatively easy to clean, and should allow for only minimum carryover from sample to sample. As a matter of quality control, the volumes of the various containment apparatuses should be checked upon their delivery (see Section 2.2.3).

The analytical instrumentation should provide the desired levels of repeatability (precision) and detectability (the appropriate signal-to-noise ratio at a particular sample level) and should also be designed to result in the minimum amount of carryover from sample to sample. Finally, the instrument should be relatively easy to clean and maintain. As a matter of quality control, the instrument should undergo a thorough evaluation upon receipt, including running it through an electronic checkout procedure (normally provided in the manual) and "running" a standard curve using well-characterized samples.

Care must be exercised in the purchase of chemical reagents. Reagent-grade chemicals often contain significant levels (ppm) of trace metals and other impurities. In certain cases, specially purified reagents may be required. Once delivered, reagents should be checked for purity by preparing control or blank samples and analyzing in the normal manner. This quality control procedure should be done prior to any actual analyses (at which time blanks would be prepared and analyzed again). Such preliminary checking of reagent quality will allow time for reagent replacement or purification.

Each lot of organic solvent (i.e., each new batch number) must be checked for contamination. A volume of solvent equivalent to that used in sample extraction should be evaporated to dryness. The residue should be weighed; it should also be analyzed by gas chromatography. If any significant quantity of organic contamination is found, the solvent batch must be redistilled or rejected entirely. Solvents used should be Burdick and Jackson "distilled in glass" or equivalent quality. Note that use of chemicals of the specified grade does not eliminate the necessity of performing checks on the quality of each new batch of material used. However, use of high quality reagents is important to minimize the probability of acquiring unsatisfactory lots of material, which would require repurification or replacement. Sodium sulfate and silica gel used in the liquid chromatography (LC) separation will frequently require cleanup by extraction with organic solvent prior to use, as described in Section 9.4.4.

2.2.2 Cleanliness Controls

Cleanliness must be an integral part of analytical methodology if quality data are to be acquired.

The containers in which samples are held for inorganic analysis must be made of high-density linear polyethylene. They must be cleaned in the following manner:

a. Wash with Alconox detergent,
b. Rinse liberally with tap water,
c. Rinse with 1:1 concentrated sulfuric acid and nitric acid mix, and
d. Rinse liberally with distilled water.

Samples for organic analysis, including CH_2Cl_2 extractions, must be shipped in amber glass bottles that have been cleaned by the above-described method adding the following steps:

e. Rinse with methanol,
f. Rinse with methylene chloride, and
g. Dry in a filtered, clean, hot air stream from an oilless compressor or place in an oven at 40° C (104° F).

Caps for containers holding organic analysis materials shall be lined with Teflon. Perform preliminary testing on appropriate aqueous and methylene chloride control samples held in a manner simulating shipment to insure that no contamination arises from this procedure. Do not use Teflon tape to seal these containers because this product contains potential contaminants.

Except for the SASS train components, all portions of the sampling apparatus that come into contact with the sampled stream should be cleaned using the same procedure that was used in cleaning the container for that sample. Such cleaning is to be performed both before the sampling apparatus is used for the first time and after a sample is acquired.

After the apparatus has been cleaned and dried, it should be stored in boxes to prevent spurious contamination. As a matter of quality control, a control sample (e.g., some test reagent) should periodically be taken into the sampling apparatus and then analyzed for contamination.

Of special concern during the sampling process itself is the accidental acquisition of substances at the sampling site that are not representative of the sample. Examples of such substances would include corrosion products, particulate matter adhering to a sampling port, or a scum floating on some liquid to be sampled. All members of the sampling team must be alert to avoid these situations.

2.2.3 Reagent Formulation

Once purchased, chemical compounds must be maintained at the desired level of purity. Chemicals and reagents prepared from these compounds should be mixed and stored only in vessels that have been thoroughly cleaned following the procedures described in Section 2.2.2. The vessels should not lead to contamination of the sample through vessel decomposition (especially caps), leaching, or permeation of contaminants through the vessel walls. Care should be taken not to contaminate reagents. Also, deterioration may result from oxidation, deliquescence, or light-induced decomposition. A suitable quality control procedure to guard against reagent contamination is to note any significant changes in the blanks or standards prepared with these reagents.

The procedures for cleaning the XAD-2 resin prior to use are specified in Appendix B.* The quality control checks described in the appendix should be applied to each batch of resin before it is used in a field study. These controls and blanks should permit the analyst to identify the source of any background contaminant and to make corrections to the results of sample analyses. If contamination is excessive (more than 10 percent of the sample level), the source should be traced and the contamination eliminated, if possible. Note that silicones (from lubricants/sealants) and phthalates (from plastics) are major potential interferences and use of these materials must be avoided entirely in collection, storage, and handling of samples for organic analysis.

2.2.4 Metrology and Standardization

Metrology is the study of devices used for measurement and their proper operation and application, while standardization is a methodology for determining the response of some particular instrument to a well-characterized sample. Metrology is of principal concern to instrument manufacturers, though analysts should be alert to deficiencies and/or problems. Examples of such deficiencies would include: nonlinearity with changes in instrument sensitivity settings, meters that are difficult to read, and electronically "noisy" phototubes or photomultipliers. Standardization is fully the responsibility of the analyst and will be the principal focus for this section of the chapter.

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*Resin not utilized within 2 months should be retested. Resin not meeting the specified criteria must be recleaned to meet these requirements before its use.

Little in the way of standardization is available for sampling. Calibration of sampling apparatus volumes should be done as a part of procurement quality control. Calibration of flow meters on sampling devices should be carried out regularly as a part of procedural quality control and quality assurance (see Sections 2.3 and 2.4).

A very important part of standardization is choosing and/or preparing reagents to serve as standards. Reagents for standardization, such as certain gaseous samples, may be purchased ready to use. Other reagents are either not available as standards, or may be too expensive to use on a regular basis. In these latter cases, standards must be prepared and subsequently verified by some appropriate means. One way to verify laboratory-prepared standards is to analyze them against primary standards such as those available from the National Bureau of Standards (NBS) or the American Industrial Hygiene Association (AIHA). Table 3 contains a list of various suitable standards. If primary standards are not available, laboratory-prepared standards may possibly be verified by analyzing the standards by several different means. Once verified, the standards should be reverified on a regular basis as they may become contaminated and/or degrade. Such reverification may be considered a quality control procedure.

The standard inorganic gases can be purchased from the NBS, as indicated in Table 3. Commercially available permeation tubes can provide a good primary standard for gas liquid chromatography (GLC) analysis if the devices are gravimetrically calibrated using NBS or ASTM traceable certified weights as a reference. The availability of certified gaseous organic standards (bp $<100°$ C) is more limited. NBS methane and propane standards are available. Others will have to be prepared and verified by other means, e.g., quantitative or elemental analysis. In using gaseous standards, one must take care that unwanted dilution does not occur, or that if mixtures

TABLE 3. LIST OF CALIBRATION STANDARDS

Available NBS – SRM

SO_2/N_2	cylinder
C_3H_8/air	cylinder
CH_4/air	cylinder
CO_2/N_2	cylinder
CO/N_2	cylinder
NO/N_2	cylinder
O_2/N_2	cylinder
NO_2 Permeation Tube	

Trace metals in coal
Trace metal in fly ash
Trace metal in fuel oil
Hg/H_2O
Trace metals/orchard leaves
Trace metals/bovine liver

Commercially Available Permeation Tubes

Bromine
Ethylene oxide
Acetaldehyde
Chlorine
Hydrogen fluoride
Cyclohexane
Hexane
Benzene
Toluene
Ammonia
Sulfur dioxide
Hydrogen sulfide
Methyl mercaptan
Dimethyl disulfide
Propane
Propylene
n-Butane
Carbon tetrachloride
Freon – 11
Freon – 12
Carbonyl sulfide
Dibutyl sulfide
Diethyl sulfide
Dipropyl sulfide

Wastewater Standards*

Minerals
Calcium
Magnesium
Sodium
Potassium
Alkalinity
Sulfate
Chloride
Fluoride
Total dissolved solids
Total hardness
pH
Conductance

Nutrients
Ammonia – N
Nitrate – N
Orthophosphate – P
Total Kjeldahl
Total – P

Demand
B.O.D.
C.O.D.
T.O.C.

Trace metals
Aluminum
Arsenic
Beryllium
Cadmium
Cobalt
Chromium
Copper
Iron
Mercury
Manganese
Nickel
Lead
Selenium
Vanadium
Zinc

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*Available from: U.S. Environmental Protection Agency
Environmental Monitoring and Support Laboratory
Quality Assurance Branch
Cincinnati, Ohio 45268

are being prepared, diluted mixtures are verified. Also, the purity of individual components used to prepare a mixture must be documented. Certain elemental and anion standards are available from either the NBS or EPA (see Table 3). Such standards are not difficult to prepare in the laboratory due to the commercial availability of relatively pure metals and salts. In preparing mixtures of standards, one must be careful of interactions that might lead to preferential loss; for example, some metal sulfate mixed with a barium salt. In preparing mixtures of standards, one must be wary of components added in large amounts having levels of contamination that could interfere with other components of the mixture introduced at low concentration. Standards below 10 ppm must be prepared fresh daily. They should be stored in dark, clean containers. Sub-ppm standards should always be prepared and stored in vessels reserved for this use. These vessels should have received pure water rinses and rinses with the standard solution before use.

2.2.5 Sampling

Level 1 sampling techniques have been selected to provide a good approximation of the true levels of the gases, liquids, or solids sampled. They are being employed here in a survey application and not in a protracted, intensive study of the source. Information gained from the Level 1 survey approach will be used as an indicator of the total source emissions. As such, poor sampling technique could easily lead to an immediate error factor of 2 to 10, which, when combined with the error factor of the measurement procedure, means that the Level 1 assessment goal will most likely not be achieved for the source.

Gases should be acquired in clean, calibrated sampling devices. If possible, the sample holding device should be evacuated prior to sample acquisition, or, at the very least, purged with several volumes of the gaseous sample before a final sample is acquired. Another concern is the homogeneity of the process stream, flue, or enclosed atmosphere from which the sample is taken. Stratification of gases does occur readily and every effort should be made to sample from a point where mixing is maximized, such as turbulent regions after restrictions. In acquiring samples, care should be taken that debris at or around the sampling point does not accidentally enter the sample vessel.

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The SASS train and the Fugitive Assessment Sampling Train (FAST) present special sampling techniques because they are complex and are used to acquire both gaseous and solid samples. An extremely important consideration in using these devices is that they be thoroughly cleaned before use. While using the devices, one must be wary of clogging of any part of their complex "plumbing." Also, flow rates must be carefully monitored and controlled during a sampling run. Samples from the SASS and FAST trains must be removed carefully under clean conditions. Containers for sample storage and shipping should be thoroughly cleaned and properly sealed after loading. Appropriate containers for SASS samples are listed in Table 4.

Liquids in process and waste streams may not mix well, making representative sampling difficult. Every effort should be made to sample where the liquid is most homogeneous or to take samples from several points and combine them. Sample containers must be clean and nonreactive (See Table 12, Chapter 6). The sampling device should be rinsed with several portions of the liquid of interest before an actual sample is acquired.

Solids tend to be even more heterogeneous than liquids. Thus, great care must go into selecting a sample. If some bulk solid, such as a waste pile, shows major heterogeneity, then a composite sample is necessary. (A composite sample is always preferred.)

Sample handling is a general concern no matter what the sample type. Once the sample is collected, care should be taken that it does not chemically or physically change other than by approved procedures (see Table 12, Chapter 6), that it does not become contaminated, that no portion of the sample is lost, and that the sample does not become diluted. Reactive samples such as the sulfur and reduced gases should be protected from light, kept warm (without condensation), and analyzed as soon as possible (within ½ h). Containers for shipment of aqueous metal ion samples should be acid-rinsed prior to use so as to prevent loss of trace metal ions to the container wall. Stabilization of liquid and slurry samples (as described in Chapter 6) is necessary and should be carried out consistently. One type of solid especially difficult to handle is particulate material on filters. Loss is to be avoided by using shipping containers that seal in such a way that loose particulate material will not pass through the seal or become lodged in the seal joint. One suggested method is to roll the filters up

TABLE 4. A SUGGESTED FORMAT FOR SAMPLE CODING AND IDENTIFICATION

Sample code	Container	Size	Sample description
1C	Amber glass	100 mL - WM	1-3μ cyclone catch
3C	Amber glass	100 mL - WM	3-10μ cyclone catch
10C	Amber glass	100 mL - WM	> 10μ cyclone catch
PF-a	Tight-sealing glass tube	250 x 24 mm	Particulate filter(s)
PR	Amber glass	500 mL	CH_2Cl_2/Methanol probe and cyclone rinse
MR	Amber glass	500 mL	CH_2Cl_2 organic module rinse
XR	Amber glass	500 mL	XAD-2 resin
XRB	Amber glass	500 mL	XAD-2 resin blank
CD-O	HDLP*	500-1000 mL	Neat condensate
CD-LE	Glass	500 mL	CH_2Cl_2 extract of condensate
CD-AE	HDLP	1000 mL	Acidified, extracted condensate
HM	HDLP	500 mL	HNO_3 module rinse
HMB	HDLP	250 mL	HNO_3 blank
HI	HDLP	2 L (+ 1 L)	First (H_2O_2) impinger--Special handling
HIB	HDLP	1 L	First (H_2O_2) impinger blank--Special handling
AI-1B	HDLP	500 mL	2nd (First APS) impinger blank
MCB	Amber glass	500 mL	CH_2Cl_2 blank
MMB	Amber glass	500 mL	CH_2Cl_2/Methanol blank
FF	HDLP	500 mL	Liquid (oil) fuel feed
CF	HDLP	1 gal	Solid (coal) fuel feed
FA	HDLP	1 gal - WM	Fly ash
BA	HDLP	1 gal - WM	Bottom ash

*HDLP = high density linear polyethylene.

and place them in a long test tube that can be tightly capped with a glass or Teflon plug.

A major problem in sample acquisition, handling, and analysis is sample identification. To minimize sample mixup and to make data treatment more efficient, it is suggested that a comprehensive sample coding system be adopted. The format code suggested would include the following:

a. Site code (e.g., Acme Power Station would be APS);
b. Contractor code (e.g., John Doe Engineering would be JDE);
c. Sample code (from presite survey; see Table 4);
d. Date of sample acquisition; and
e. General sample number.

An example identification number would thus be:

APS-JDE-1C-6/8/78-22130.

This same code number should be used from sample acquisition through final data tabulation.

2.2.6 Procedures

Suitable laboratory techniques are an essential part of sample preparation. Digestions, extractions, or combustions should be carried out in a vapor-free laboratory. Any reagents (e.g., HNO_3, HCl, acetic acid, benzoic acid) or solvents to be used in these processes should be checked for purity before use. These reagents may need to be purified using such techniques as distillation, zone refining, and recrystallization. Concentration through solvent evaporation must be performed without contamination of the sample.

The grinding apparatus for solids must not contribute to the sample. For example, carbide rather than steel blades should be used in any blender-type device. Of course, significant effort must be made to assure that there is no sample carryover from one grinding operation to the next.

Personnel should be thoroughly trained in the basics of the analytical procedure(s) they are to use. This training should include imparting a thorough knowledge of the operation of any instrumentation to be used. Quality control procedures will measure the success of this training. More difficult to instill is an alertness to procedures not working as they should. To develop such alertness, dialogue on ways to improve all aspects of the procedures should be encouraged.

Cleanliness must also be of concern when using instrumentation. Instrumentation must not be exposed to corrosive materials that could cause instrument degradation and/or failure. Instrument-associated sample containers must be kept clean and sample carryover avoided. For example, syringes and cuvettes should be rinsed several times with the sample to be analyzed. In general, the equipment and the place of analysis must be maintained in a clean and orderly manner. The laboratory temperature and humidity should be kept reasonably constant.

An essential aspect of Level 1 techniques is the analysis of control samples. The control sample and its handling throughout the laboratory sequence should be identical to the real sample and its handling. For instance, an unexposed XAD-2 cartridge must be dumped, homogenized, and a 5-g aliquot reserved for the Parr bomb ashing and trace element assays. The remainder must be Soxhlet extracted and the extract subjected to the entire organics analysis sequence. Similarly, for every type of analysis performed there should be a control sample analysis performed periodically.

Another good laboratory practice is that of testing for matrix effects, those interactions between the species of interest and some other component(s) of the sample that lead to high or low analytical results. The presence of matrix effects leading to low analytical results can be easily ascertained by the method of multiple standard additions. This procedure should be carried out with several test samples every time a new type of sample matrix is encountered. If no matrix effects are detected, the analysis can proceed using a standard curve. If significant matrix effects are detected, all analyses must be carried out using the method of standard additions. Matrix effects leading to high results are more difficult to identify. One way of doing so is to analyze the sample by two or more methods, each of which is based upon a different physical and/or chemical property of the substance of interest. High background, resulting from a component of the sample and not the reagents added to it, may also lead to high analytical results. The availability or development of a true blank is one way to identify and deal with this problem; multiple method analysis is another. A false high result will not be as serious in a Level 1 assessment as a false low result because a false high result will trigger a call for a Level 2 assessment wherein

TABLE 5. METHODOLOGY CALIBRATION CHECK

Methodology	Check rate Multipoint Weekly	 Each analysis session	 Three points--center and bracketing points Each analysis session
IC	√		√
Test kits		√	
AAS		√	
GC	√		√

more accurate analytical methodologies should lead to its discovery. The conclusion is that false low results due to matrix effects must be tested for and dealt with; testing for false high results due to matrix effects or high backgrounds should receive only a moderate amount of attention.

A fourth general concern is calibration, or development of a standard curve. Once an instrumental system is functioning properly, a multipoint standard curve should be acquired. The accuracy of this curve should be checked using NBS, ASTM, or EPA standards. The frequency of checking the standard curve (single point or multipoint check) depends upon the methodology, as some are more susceptible to drift than others. Table 5 indicates the minimum time interval between checks for each methodology.

For SSMS, a single control sample should be prepared and analyzed during each analysis session. Accurate results will indicate that the instrument is operating in a stable manner.

Good laboratory procedures associated with the specific analytical techniques used in the Level 1 program are discussed below.

2.2.6.1 Spark Source Mass Spectrometry--

It is apparent that the accuracy and precision of spark source mass spectrometry (SSMS) will be limited by the exposure factor used in the "just disappearing line" quantification procedure (see Chapter 8). The other major sources of variation are electrode preparation, the sparking process, and photoplate development. Uniform electrodes can be obtained with thorough mixing of finely ground solid samples and graphite. Liquid samples are mixed with graphite and taken to dryness, then slurried and dried again before finally milling them thoroughly in dry form and forming an electrode. Good techniques in photoplate development, including using fresh reagents and controlling development bath temperatures, are also necessary. Internal standards are always included in these samples. One has to assume that the internal standard will behave similarly to the unknowns; that is, it will distribute like the unknowns on and among the graphite particles and ionize with an efficiency equal to that of the unknowns. Checks of the internal standard should be run at least once a month against the mass and molar response of another standard sample, i.e., elements in an NBS-defined sample. Any gross changes in this response will indicate that something is wrong either with the instrument or with the internal standard.

2.2.6.2 Ion Chromatography--

This is a relatively straightforward technique, the number of experimental variables being minimal. The principal analytical concern while performing ion chromatography (IC) is the introduction of contamination. To avoid contamination, columns must be thoroughly cleaned before use and then equilibrated with very pure eluting solutions. Appropriate controls and a standard concentration series should be included in the daily runs as standard operating procedures.

2.2.6.3 Water Test Kits--

Water samples may be analyzed in the field using commercial test kits. Little can go wrong with the mechanics of these test kit procedures; however, interferences are a real possibility in that the test kits are usually rather simple chemical systems. Standard addition tests should be performed if interferences are at all suspected. False low results at this stage of the phased approach for environmental assessments are much more serious than false high results.

2.2.6.4 Atomic Absorption Spectrometry--

The cold vapor and hydride complex techniques are used to generate the gaseous forms of Hg, Sb, and As for measurement by atomic absorption spectrometry (AAS). Great care must be taken to see that the gas-generating systems do not become contaminated and that there is no retention of previously generated gases. Control samples should be measured after every five or ten field samples. Care must be exercised to see that none of the generated gaseous sample escapes before entering the AA system. Newer atomic absorption spectrometers are quite stable electronically, and measuring an absorption signal due to cold Hg vapor is done with minimum difficulty. The analysis procedures used for As and Sb are characterized by more significant sources of variation and error. As a matter of good laboratory practice, a multipoint standard curve should be acquired along with each set of unknowns analyzed. Also, it is good practice to run a single point standard after five to ten unknowns have been analyzed to assure that instrument drift or sample input blockage has not occurred.

2.2.6.5 Colorimetric Method for NO_x Analysis (Method 7) (refs. 4, 5)--

Method 7 consists of three primary steps. First the NO_x gases are collected and reacted in an acidic, oxidizing medium to produce a nitrate ion. The nitrate ion is then reacted with phenoldisulfonic acid to produce 6-nitrophenol-2,4-disulfonic acid. Finally, the free base form of this latter acid is measured colorimetrically. Special care must be exercised at several points in this multistep procedure. First, condensation of water in the gas collection system must be avoided. The introduction of particulate matter into the sample flask must also be avoided as such particulate matter might contain nitrates, which would result in erroneously high NO_x valves.

A sufficient quantity of oxygen is necessary for conversion of NO to NO_2. If this is not present in the original sample, it must be introduced. In so doing, care must be exercised so that sample is not lost nor interferences introduced. Great care must be exercised in measuring the sample flask pressure before and after reaction of the NO_x gases with the acidic, oxidizing media. Of course, system gas leakage rates must be controlled.

Overheating during the evaporation step or the nitration step can lead to low results; heating with steam is required. Also the pH of the test and standard solutions used in the spectrophotometric step must be within 1 pH unit of one another. Finally, the wavelength setting of the spectrophotometer used must be checked for proper calibration on a regular basis.

2.2.6.6 Gas Chromatography--

Gas chromatography (GC) is to be used for both inorganic and organic analyses. One good practice is to regularly monitor the GC parameters such as column, injection port, and detector temperatures; current and/or voltage setting on detectors; and gas flow rates. Attenuation controls on the gas chromatograph should be checked as a part of instrument procurement quality control. The columns to be used are specified; hence, analytical error due to sample degradation in the column, column bleed, etc., should be minimal. All column connections should be leak-checked regularly, and the carrier gas freed of residual oxygen. Water vapor should be filtered from the air delivered to the flame ionization detector. Good injection technique is always important. A fixed volume gas injection loop should be used to facilitate gas sample injection. The septum should be replaced after every 20 to 50 injections of liquid samples.

2.2.6.7 Liquid Chromatography--

Liquid chromatography (LC) demands great care in column packing. The packing should be homogeneous with no cracks or bubbles present. The packing material itself must first be thoroughly cleaned with organic and aqueous solvents, and then rinsed in contaminant-free pentane and methanol prior to activation. Careful placement of the sample in the column is critical. The sample should enter the column as a uniform "plug" of minimum thickness. Eluting solvent should be added to the column without agitation of the sample plug. Reagents used to prepare eluting solvents must be of high purity. This solvent purity must be checked by the appropriate blank determination techniques prior to use. See Section 9.4.4.1 for more detail on column preparation.

2.2.6.8 Infrared Spectroscopy--

This qualitative tool is used to determine the predominant classes of organic compounds present. The major error sources of this technique are associated with sample handling. Salt plates and cells must be kept free of contamination, including moisture and sample carryover. Infrared (IR) work should be done in a low humidity, dust- and fume-free environment. As a control, empty cells and plates should be analyzed with each sample series. One further concern is wavelength calibration; a standard polyethylene film should be analyzed daily as a calibration check.

2.2.6.9 Low Resolution Mass Spectroscopy--

Low resolution mass spectroscopy (LRMS) is to be used to indicate the presence of different types or classes of compounds, and, if possible, the presence of particular compounds. A skilled operator is necessary in order to maintain an LRMS system; also, a mass spectroscopist will be needed to interpret the data since such interpretation may be a matter of pattern recognition and analysis. Good laboratory practice dictates that the mass calibration should be checked at least once a week.

2.2.6.10 Morphology--

This technique is used for characterizing particulate sample collected as part of a Level 1 assessment. In the area of particle morphology, good laboratory practice begins with sample acquisition. There should be a minimum of handling and manipulation of materials during the sample-taking steps, since increases or decreases in size or aggregation may result. Care must be exercised in protecting samples from introduction of extraneous materials. It is preferable to view sample material as soon after acquisition as possible, if only to obtain an initial photograph and observation. This evidence will serve as a reference to change with passage of time. The microscopist should make frequent references to standard known materials when making judgmental determinations on matters such as crystal systems, surface characteristics, refractive indices, etc. At least every tenth sample should be analyzed by another microscopist as a quality control check.

2.2.6.11 Biotests--

These tests can be categorized into two general types: (a) those attempting quantification of test sample ecological effects, and (b) those giving indication of possible health effects. The list of good laboratory practices to be used in biotesting is long and complex. A discussion of all these practices is beyond the scope of this chapter. For more detailed information refer to Guidelines for Environmental Assessment Data Quality Programs (ref. 3, pp. 59-65).

2.2.7 Subtraction of "Blank" Background Values

It has been determined that there is no single, accepted definition among IERL/EPA contractors for the term "blank." To some, "blank" refers to the signal due to the total amount of species of interest found in reagents, glassware, and instrumentation used to analyze an actual test sample. To others it refers to the general background signal that could arise from species of interest, other chemical interferences, or instrumental components, as for example, stray light. In this manual, we will adopt the more restrictive definition, as it allows a more precise explanation of the sources of measurement difficulties.

A measurable "blank" then is a signal (above some nominal baseline) due to the actual presence of some amount of the species of interest. An "interference," on the other hand, is a signal above the baseline due to a species other than the one of interest; by definition, it overlaps the signal from the species of interest. The "baseline" itself is the third type of background. This nonzero signal is usually not discrete or "peaked," but is generally horizontal; it is usually due to instrumental parameters such as unbalanced amplifiers, electronic drift, stray light, etc.

During the analysis of an actual test sample, these three sources of background are dealt with in different ways. The "baseline" signal is to be subtracted from the test sample signal prior to calculation of test sample concentration. The "blank" signal value is used to calculate a concentration or mass that is subtracted from the test sample concentration or mass. An interference, on the other hand, is usually difficult to deal with. Numerical resolution of the signal due to the interference and that due to the species of interest is a possibility, though it is not very probable with the types of sample matrixes found in Level 1 work. If the species interfered with is of environmental concern, it may be necessary to use another technique for the analysis. In the case of an unresolved interference, the final analytical result should be designated "I".

Examples of a baseline, a test signal, a true blank signal, and an interference and test signal combined are given in Figure 5. The baseline-corrected blank and test signals are simply $I_t - I_{bs}$ and $I_{bl} - I_{bs}'$, respectively. If we assume that the relation between signal and concentration is simply $C_i = kI_i$, then the true test concentration is given as

$$C_{t,corrected} = k(I_t - I_{bs}) - k(I_{bl} - I_{bs}').$$

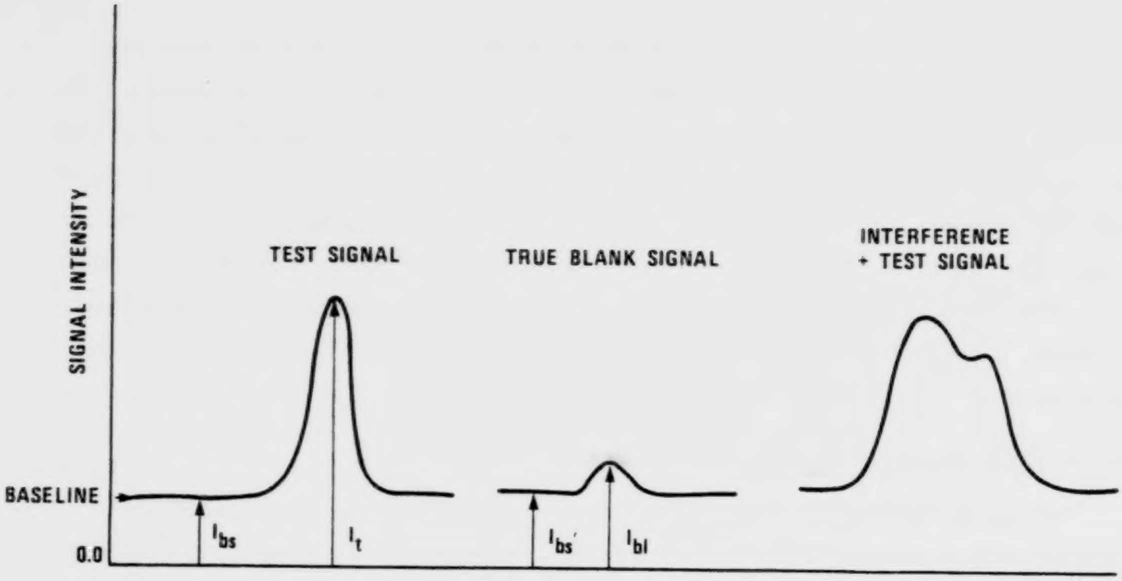

Figure 5. Examples of baseline, test signal, true blank signal, and interference + test signal.

For some analytical determinations made under certain matrix conditions, there may be an interference that is strongly negative, and the test sample signal will thus fall below the blank and/or normal baseline signal. In this case, the final analytical result should be designed "NG" (for negative).

2.2.8 Limits of Detection

The limit of detection is calculated from the uncertainty, indeterminate error, or "noise" in either the "blank" signal value, or the "baseline" signal value measured at maximum instrumental or procedural sensitivity. A positive or negative interference prohibits the calculation of a meaningful limit of detection value.

The uncertainty or noise value can be determined in three ways. First, several replicate blank or baseline signals can be measured and their standard deviation calculated. A second approach is to determine the standard deviation of the intercept of a calibration curve by means of linear regression analysis; that is, to calculate σ_b for $y = mx + b$. Finally, one can estimate visually the noise level of a signal. There is some disagreement as to the relationships between the uncertainty of the blank or baseline signal and the lower limit of detection. Generally accepted, though, is the definition of lower limit of detection being that concentration or mass that would give rise to a signal two times the standard deviation of the blank or baseline signal. For those cases where σ of the background cannot be calculated, the limit of detection is defined as that concentration or mass that will give rise to a signal equal to the peak-to-peak noise of the baseline or blank. This is the concentration or mass that gives a signal-to-noise ratio of 2.

2.2.9 Data Computation and Reporting

Suitable laboratory techniques in this area involve avoiding data interpretation errors, calculation errors, and errors in recording calculation results.

Data interpretation error, in this case, refers to using the wrong model for a calculation. For example, one might assume a linear response at the high or low end of a particular concentration range when, in fact, this is not true. As another example, one might assume that a particular multiple standard addition curve is linear when, in fact, it is not. This kind of error is especially dangerous when microcomputers and minicomputers are used to produce the end result and the raw data are seldom seen. It is imperative that response (standard) curves be periodically plotted and studied to be sure that the correct calculation model is being used.

Calculation errors can be controlled by good laboratory practice and good quality control; that is, a calculation should be carried through using data that have already been analyzed and for which the correct results are known.

Recording errors are not uncommon. The best way to control these is through conscientious verification of each number or other result recorded regarding its accuracy and where it is recorded. Having available well-designed calculation and tabulation sheets (examples are presented throughout this manual and in Appendix A) will help to minimize math and recording errors. All results that are reported in a study should be independently checked for their correctness before release of the data.

2.3 QUALITY CONTROL

As noted in the previous section, good laboratory practices and quality control are often inseparable. There are, however, several QC procedures that involve management and that allow management to judge the SLT and QC procedures performed by the analytical staff.

The first of these procedures involves management and staff working together to plan the SLT/QC/QA program. Such a plan would cover all aspects of acquiring quality data, including:

a. Development of checklists of SLT/QC procedures to be followed in each aspect of sampling and analysis (see Table 6 for sample checklist).

b. Delegation of responsibility for implementing SLT/QC procedures.

c. Designation of lines of communication between management and analytical staff for reporting concerns about weaknesses (or excesses) in certain SLT/QC procedures.

d. Delegation of responsibility for in-house review of data and calculations.

e. Formalization of procedures for continued review and improvement of the SLT/QC program.

TABLE 6. CHECKLIST FOR ANALYSIS FOR Hg USING AAS

1. Excess H_2O_2 decomposed. ____________
2. Hg° generation system clear of old sample. ____________
3. Proper wavelength and lamp current selected. ____________
4. Blank obtained. ____________
5. Multipoint calibration performed. ____________
6. Check performed for volatile organic materials absorbing at 253.7 mm ____________
7. Standard and sample absorbances verified ____________

Another QC procedure to be employed by management alone is periodic onsite inspection. The inspection would be for purposes of verifying that those SLT and QC procedures listed on the checklists are being performed and are sufficient.

A third procedure would be for management periodically to collect running reports of instrument readings for blanks and select calibration and/or control standards. That is, each time an analysis session is held, the instrument readings obtained with blanks and select calibration or control standards should be recorded on a graph or such values plotted against analysis session number (Shewhart quality control chart or equivalent). This running plot should be submitted on a weekly basis to management for review. Any abrupt or even gradual changes in these values that cannot be explained by some change in procedure is grounds for suspicion of changes in data quality, and, accordingly, should trigger an investigation.

One final procedure is for management to periodically submit (e.g., once a month) select, blind test samples for analysis. Such samples might be NBS, ASTM, or EPA standards. These blind test samples might also take the form of replicates of a single sample, the analyses of which would provide a measure of precision. An alternate approach to that of using blind samples is to submit portions of samples to other laboratories for analysis. This yields a measure of precision (between laboratories). There is no guarantee, however, that the other laboratories will do work that is any more accurate than that done in the home laboratory.

2.4 QUALITY ASSURANCE

The analytical staff is to monitor the quality of its work through various SLT and QC procedures. Management is to further monitor quality through QC procedures carried out in cooperation with the analytical staff. Quality assurance (QA) is an independent monitor of the quality of work performed, but, in this case, the procedures are carried out by an independent group in cooperation with both management and the analytical staff.

There are several procedures that the QA group will perform. The first of these is to review the SLT/QC plan as conceived by management and the analytical staff. This should be a critical review through which weaknesses and excesses will be noted.

Another activity will involve the performance of onsite inspections to observe the implementation of analytical methodology and the SLT and QC procedures. The same checklists utilized by management are to be used here. The value in having two groups, management and QA personnel, check for performance of desired procedures is that one group may note weaknesses missed by the other. In addition, the independent QA personnel will most likely be more objective in their judgments.

A third QA procedure is for QA personnel to analyze portions of the samples collected by the analytical staff. The QA personnel should have equipment and expertise available to perform state-of-the-art analyses that should lead to analytical accuracy well within the bounds imposed by the Level 1 Assessment Program. Comparisons of results obtained by analytical staff and QA personnel should indicate effectiveness of SLT and QC procedures.

As an alternative to the third QA procedure, QA personnel can provide the analytical staff with select, blind test samples. Again, these may be NBS-, ASTM-, or EPA-certified standards, or well-characterized standards prepared by QA personnel.

2.5 CONCLUSIONS

Suitable laboratory techniques, quality control, and quality assurance, then, are the three programs that should lead to data quality meeting the goals of the Level 1 Assessment Program. Strict adherence to these programs will maximize the accuracy and suitability of study data. Indeterminate errors in sampling; unknown and uncharacterized sample matrix effects; and unknown, indeterminate errors in analytical techniques offer an ever-present possibility of poor quality data despite the above precautions. For these reasons, SLT, QC, and QA procedures must be continually evaluated and improved, and this evaluation and improvement must be concurrent with evaluation and improvement of analytical methodologies.

CHAPTER 3

SAMPLING AND ANALYSIS OF NON-PARTICULATE-LADEN GASES

3.1 INTRODUCTION (refs. 6-12)

This chapter covers the general sampling methodology and measurement techniques to be used in the field for determination of the organic (bp <100° C) and inorganic gaseous samples. The methods are as detailed as possible, but it should be realized that not every detail for every source can be covered. It is important, therefore, that the personnel involved in the field effort be well trained and experienced. Moreover, obtaining a representative sample from a simple gaseous stream can be complicated by stratification from incomplete mixing or by variations in stream components over a period of time. Generally, gaseous samples are obtained from the process vents and effluent streams either by a grab sample technique or by an integrated sampling train, but for the purpose of Level 1 assessment, a single 1- to 2-h integrated sample is sufficient. Careful planning is also necessary to insure that sample acquisition is made at a reasonably representative point (position and time) in the stream or process cycle.

The details of the sampling guidelines and sampling techniques are briefly discussed in Sections 3.3 and 3.4, respectively. The details of the onsite analysis of inorganic gases (NO_x, CO, CO_2, O_2, N_2, and sulfur gases) and organics (bp <100° C) are presented in Sections 3.5, 3.6, and 3.7. Data report forms for sampling and measurements in the field are presented in Appendix A.

3.2 SAMPLING METHODOLOGY

This chapter briefly discusses the sampling methodology for gases emitted from the following stream types:

a. Process streams,

b. Vents, and

c. Effluents.

3.2.1 Gaseous Process Streams

Gaseous process streams refer to contained, non-particulate-laden gases being transported from one area to another. These streams exist under conditions that range from a slightly negative pressure to highly pressurized pipeline systems. Also, the contents of gaseous process streams range from corrosive and toxic process effluents to complex organic mixtures. For the purposes of source assessment, only those streams that are either influents to (input water, gas, fuel, etc.) or effluents from the process are considered for sample acquisition. Consequently, internal process streams are seldom of concern since they do not constitute influents or effluents in contact with the environment. Exceptions to this rule involve such streams existing prior to control devices or being held for interim periods prior to discharge, such as holding or surge systems situated in-line prior to flare discharge. Fugitive leaks of gaseous materials are discussed in Chapter 5.

3.2.2 Gaseous Process Vents

Gaseous process vents are generally found in tank farm areas or in various system operations requiring pressure surge variability.

3.2.3 Gaseous Process Effluents

Gaseous process effluents refer to those gases exhausted into the atmosphere from ducts or flues. For the purposes of this chapter, gaseous organic species with boiling points less than 100° C and inorganic gaseous effluents from these units are considered. The particulate matter content along with higher molecular weight organics are obtained via the Source Assessment Sampling System, which is discussed in detail in Chapter 4.

3.3 SAMPLING GUIDELINES

This section briefly describes the problems and considerations involved in sampling process streams, flues, ducts, and vents.

3.3.1 Process Streams, Flues, and Ducts

Careful planning is needed for the selection of the most representative sampling point. Frequently, pipeline, duct, and vent systems consist of composite streams wherein the main or primary stream is joined in one or more places by secondary streams. When this is the case, a sampling point must be chosen far enough downstream of the joint to insure component homogeneity. An optimum choice for sample withdrawal in a gaseous system is at a point downstream from a bend in the pipe or duct, since a bend induces turbulence and therefore homogeneity.

In-line valves or sampling ports must also be assessed for their compatibility with available apparatus. For example, the process port or valve entrance will in many cases be larger than the probe diameter. To solve this problem, a series of one-hole stoppers of various size increments or gland-type valves may be used to fit over the probe and seal the port entrance.

3.3.2 Vents

Vent systems generally consist of relief tubes or exit ducts regulated by in-line pressure release valves. Vents are found in holding tanks and storage tanks and usually discharge into the air when the tank pressure exceeds the pressure setting of the in-line valve. The velocity of the gases being emitted from vent systems as well as the time duration of the vent cycle are directly proportional to the diameter of the vent tube, the headspace volume of the system being vented, and the pressure setting of the in-line relief valve.

Units or tanks with pressure vent releases to ambient air are sampled with a grab gas sampling train (Figure 6). The important considerations in obtaining vent gas samples are:

a. The sample must be taken while the vent cycle is in progress. (Cycle periods for individual processes should be known as a result of the pretest survey.)

b. The probe should be situated so that a representative sample of the vent effluent is obtained without dilution by ambient air.

3.4 GAS SAMPLING TECHNIQUES

All except fixed gas samples must be taken in glass bulbs. The reactive sulfur and nitrogen gas samples should be collected quickly and analyzed immediately. Fixed gas samples may be collected by using an integrated gas sampling train (see Section 3.4.2). These two methods are discussed in this section.

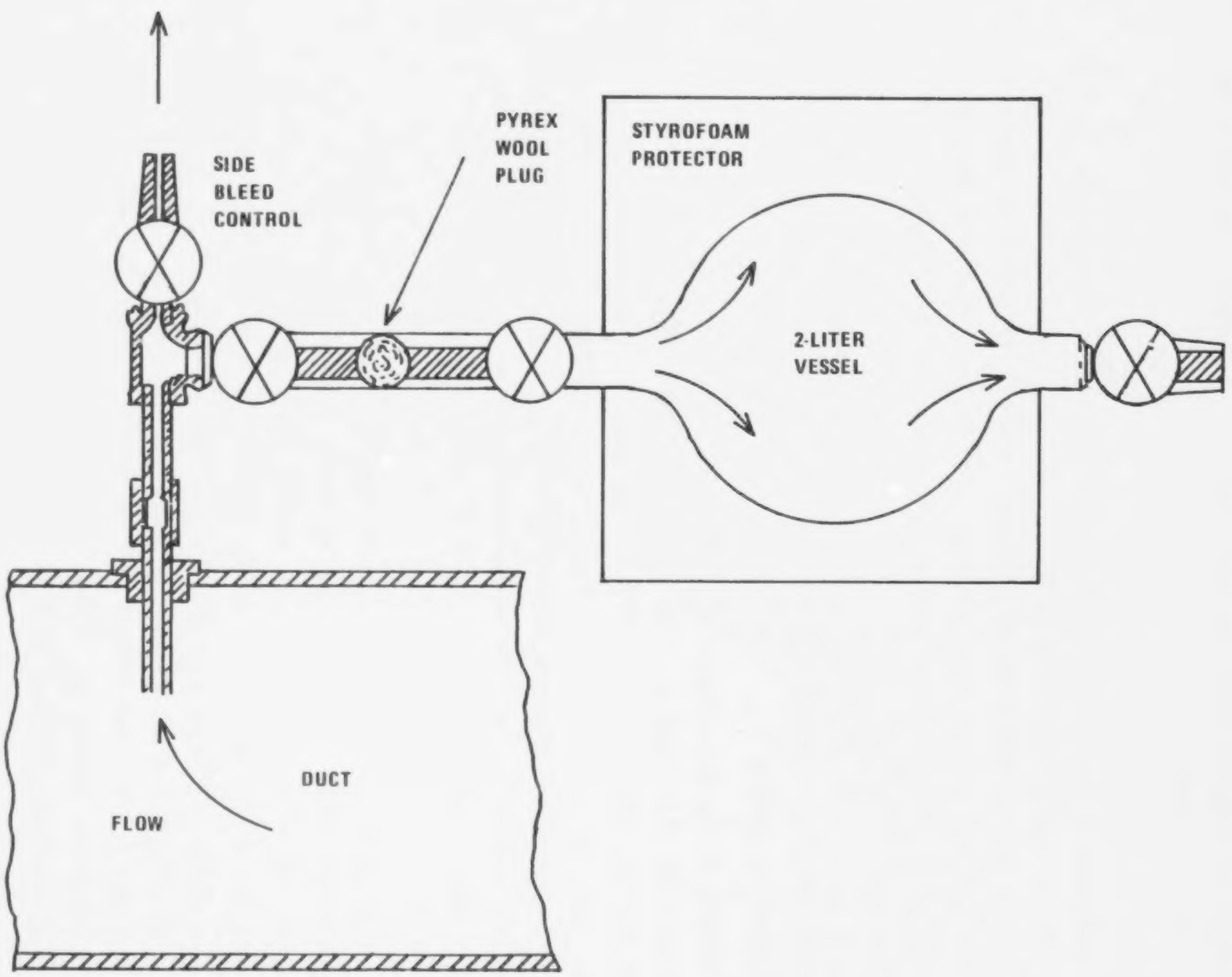
SIDE
BLEED
CONTROL
PYREX
WOOL
PLUG
STYROFOAM
PROTECTOR
2-LITER
VESSEL
DUCT
FLOW

Figure 6. Grab sampling apparatus.

3.4.1 Grab Gas Sampling (refs. 13-20)

Gaseous grab samples may be taken in one of three ways, depending on the pressure of the stream in question: high pressure line, slight positive pressure grab, or negative pressure grab samples. The basic sampling bulb is illustrated in Figure 6.

3.4.1.1 High Pressure Line Grab Samples--

The apparatus illustrated in Figure 6 is used when the pressure is high enough in the stream to require a side-split-bleed to provide a sufficient pressure reduction for effective bulb purge. The sampling bulb is the dual valve, positive displacement type and is 2 L in volume. The bulb must be purged with approximately ten volumes of the stream gas before the sample is isolated.

A small glass wool plug is inserted in-line prior to sampling to prevent the influx of particulate matter into the bulb during the purge and sample collection periods.

3.4.1.2 Slight Positive Pressure Grab Sampling--

The positive displacement, dual valve glass sampling bulb described above may also be used in ducts, pipes, or vent systems where line pressure is slight. Because the pressure is slight, a side-bleed may not be required for pressure reduction. The pressure bleed valve is adjusted accordingly or may be totally closed. A small glass wool plug is inserted in-line before sampling is begun, and approximately ten volumes of sample gas must be purged through the bulb prior to isolation of the sample.

3.4.1.3 Negative Pressure Evacuated Bulb Sampling--

An evacuated flask or a gas sampling train, as shown in Figure 7, is used for sampling negative pressure systems or open effluent lines such as vent systems or point fugitive emissions (the latter are discussed in Chapter 5). The number of bulbs required for a given sampling effort will be known as a result of the pretest site survey (Section 3.2). The bulbs are evacuated in the field using a small vacuum pump and are then taken to their respective sites for sample acquisition. They should be checked for vacuum with a gauge immediately before sampling.

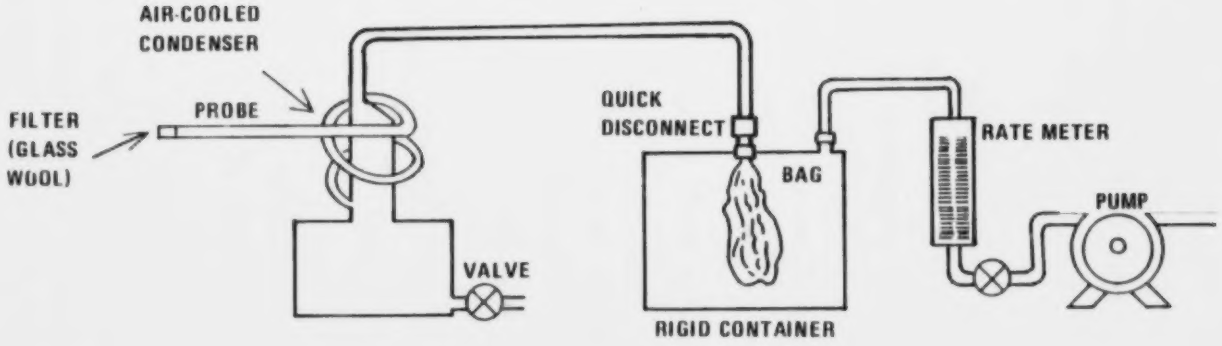
AIR-COOLED CONDENSER
FILTER (GLASS WOOL)
PROBE
VALVE
QUICK DISCONNECT
BAG
RIGID CONTAINER
RATE METER
PUMP

Figure 7. Integrated gas-sampling train.

The entrance nozzle of the bulb must be fashioned so that a probe may be attached. Supported pyrex glass, quartz, or ceramic tubing of greater than 0.6 cm (¼ in.) diameter and at least 30 cm (12 in.) in length are acceptable materials for the probe intake section. Other connecting tubing to the collection vessel must be of a similarly nonreactive material. At the time of sampling, attach the probe to the evacuated bulb, and then insert it into the vent or negative pressure duct for sample withdrawal.

3.4.1.4 General Considerations--

For safety reasons, all of the above-described sampling bulbs must be encased in a protective jacket of styrofoam. The new and used containers should be thoroughly cleaned following procedures outlined in Chapter 2, filled with nitrogen, and stored for further use. Teflon valves should be used in the sampling system. Stopcock grease should never be used.

3.4.2 Integrated Gas Sampling

The nonreactive fixed gas samples shall be taken using an integrated gas sampling train (see Figure 7). The gas sample is bled or drawn through a nonreactive probe and passed through an air-cooled condenser by means of negative pressure from a small diaphragm pump. The air-cooled condenser, or equivalent, removes excess moisture in the gas stream and also cools the hot gases. A flow rate meter is used to measure flow into the bag. The collected gas sample is then analyzed by gas chromatography or by wet methods of analysis.

3.4.2.1 Apparatus--

a. Probe: Borosilicate glass or other nonreactive material equipped with a filter (either in-stack or out-stack) to remove particulate matter.

b. Condenser: Air-cooled condenser or equivalent.

c. Valve: Needle valve, to adjust sample gas flow rate.

d. Pump: Leak-free, diaphragm type, or equivalent, to transport sample gas. Install a small surge tank between the pump and rate meter to eliminate pulsation effect of diaphragm pump on the rotameter.

e. Flow rate meter: Rotameter capable of measuring a flow range from 0 to 1.0 L/min.

f. Vacuum gauge: At least 305 mm H_2O (12 in. H_2O) gauge to be used for the sampling train leak check.

g. For fixed gases only (CO, CO_2, O_2 and N_2): Polymer sandwiched aluminized bag, or equivalent, with a capacity in the range of 10 to 30 L (0.3-1 ft^3). Bags may be reused if they are clean.

3.4.2.2 Reagents--

None.

3.4.2.3 Sampling Procedure--

Prior to field use, all bags are to be leak-checked. In the field, prior to the sampling operation, the train is also leak-checked. This is done by plugging the probe inlet and drawing a 250 mm H_2O (10 in. H_2O) vacuum on the system minus the bag. The vacumm should remain stable for at least 1 minute.

The sampling point in the duct should be approximately at the centroid of the cross section at a point preferably no closer to the walls than 1 m (3.28 ft). This is only a general rule, however, which may vary considerably depending on duct diameter. A sample is taken as follows:

a. Place the probe in the stack at the sampling point and then purge the sampling line up to the bag.

b. Connect the bag and make sure that all connections are tight and leak-free.

c. Pass the sample gas stream through an air-cooled condenser.

d. Sample at a rate to fill the bag in about 3 hours.

e. At the conclusion of the sampling interval, disconnect the bag and analyze as quickly as possible.

3.5 FIELD MEASUREMENTS (refs. 21-24)

Gaseous samples to be analyzed will come from various sources including stacks, vents, process input streams, process product streams, and ambient air.

These samples must be analyzed for inorganic species over a short span of concentrations ranging from sub-ppm levels for sulfur compounds to several percent for CO_2 and water in stack gas effluents. Because many of the samples that are taken, especially those that contain H_2S and other sulfur species, are unstable due to wall adsorption or possible chemical reaction, it is specified that the analysis be performed onsite immediately. This also eliminates the shipping of a potentially large number of bulky sample containers and permits additional sample taking if a problem area is identified.

Because no single unit is suitable for all the gaseous species, a recommended set of measurement techniques and conditions is shown in Table 7. It is not expected that the proposed set of conditions will be suitable for all mixtures and all possible concentration ranges. If a unique situation should arise, an alternative set of analysis conditions should be selected and submitted to the Project Officer and PMB-IERL-EPA for approval.

The actual onsite sampling will be accomplished by using the methods described in the previous sections. The sample will then be returned to the mobile laboratory and attached to the gas chromatograph or the appropriate instrument via a sampling valve. The sampling vessel can then be stored for further analysis at the laboratory or purged, cleaned, and evacuated for further use in the field. The actual onsite measurement techniques for inorganic and organic (bp <100° C) gaseous species are discussed below.

3.6 ANALYSIS METHODOLOGY

The concentration of total oxides of nitrogen (NO_x) in an emission stream for Level 1 is determined using EPA Method 7 (phenoldisulfonic acid method). Analysis of gas samples for inorganic components (CO, CO_2, O_2, N_2, and sulfur species) will be performed in the field by gas chromatography. The columns and appropriate conditions are shown in Table 7. The samples should be analyzed the same day they are taken and as soon after acquisition as possible. The instrument is set up with the column and conditions appropriate for the specific analysis to be performed. Retention time and quantitation calibrations are made with the proper standard gas mixture. Ammonia, hydrogen cyanide, and cyanogens are analyzed by using GC methods. Wet chemical methods are satisfactory if lower detection limits are essential. The sulfur compounds are especially prone to degradation and must be analyzed immediately after taking the grab sample in the field by the gas chromatography/flame photometric detector (GC/FPD) procedure described in Table 7.

TABLE 7. RECOMMENDED ANALYSIS OF GAS SPECIES

Species of interest	Sensitivity	Column	Temperature and conditions	Detector
CO_2, CO, O_2, and N_2	>25 ppm	a) 5 ft x 1/8 in., SS with Chromosorb 102 b) 8 ft x 1/8 in., SS 13 x Molecular Sieve c) 5 ft x 1/8 in, SS no packing	Isothermal at 40° C. When the CO_2 peak has eluted in the Chromosorb 102 column, switch to the Molecular Sieve column and obtain the remaining peaks	Dual thermal conductivity
H_2S*, SO_2*	>25 ppm	6' x 1/8" Teflon Porapak N	Isothermal at 80° C	Thermal conductivity
H_2S, SO_2, COS mercaptans and thiophene	>1 ppb†	36' x 1/8" Teflon column with 12% polyphenyl ether and 0.5% H_3PO_4 on 40/60 Chromosorb T	Isothermal at 50° C for 5 min then increase at 10°/min to 100° C. Hold for 10 min.	Flame photometric detector
NH_3, HCN, cyanogen	>100 ppm	6' x 1/8" glass Porapak Q	Isothermal at 40° C. Helium carrier gas	Thermal conductivity
NO, NO_2, NO_x	1 ppm		EPA Method 7 or in-line chemiluminescent analyzer	
Volatile organics (bp range -160° C to +30°C)	1 ppm	6' x 1/8" stainless steel or glass, Porapak Q	Helium carrier at 20 mL/min. Detector temperatures 200° C. Isothermal at 60° for 4 min, increased 20° C/min to 110° C; hold at 110°. Bake-out at 170° C as necessary between injections.	Flame ionization

See footnotes at end of table.

TABLE 7 (continued)

Species of interest	Sensitivity	Column	Temperature and conditions	Detector
Volatile organics (bp range 30° C to 100° C)	1 ppm	6' x 1/8" glass, 20% OV-101 or 100/120 mesh Chromosorb-W-HP	Helium carrier at 20 mL/min. Injector and detector temperatures: 200° C. Isothermal at 30° C.	Flame ionization

*Concentrations greater than 25 ppm only. For survey work and lower concentrations, the flame photometric detector system must be used.

†1. Exit end of column should be fitted directly into the base of the detector and any metal transfer lines should be eliminated.

2. The FPD response tends to saturate at concentrations greater than 2 ppm for a 10-mL injection volume. Injections should be repeated with smaller (1 or 0.1 mL) sample size if apparent concentration exceeds 2 ppm.

3. Detector temperatures above 130° C are reported to result in losses of sulfur species.

NOTE: SS = stainless steel.

3.6.1 Sampling and Analysis of Total Oxides of Nitrogen

As stated above, the concentration of total oxides of nitrogen (NO_x) is to be determined using EPA Method 7. This procedure involves conversion of NO_x to nitrate, reaction of that nitrate with phenoldisulfonic acid to produce 6-nitro-2,4-phenoldisulfonic acid, and colorimetric measurement of the anion form of the nitro product. Sampling consists of taking six evacuated grab samples at a point of average velocity every 30 min for a total time period of 3 h. This procedure provides a pseudointegrated NO_x value.

The method is suitable for the detection of NO_x in the range of 2 to 400 mg/dsm^3 and the sensitivity is approximately 1 mg/dsm^3. It should be noted that this method does not supply a nitric oxide value but does supply a total NO_x value that is reported as NO_2. If NO concentration is of special interest, a grab sample must be taken and immediately analyzed by some other suitable method.

Data from an in-line chemiluminescence NO_x analyzer are acceptable by Level 1 specifications.

3.6.2 Onsite GC Analysis for CO, CO_2, O_2, and N_2

During instrument setup at each new site, the gas chromatographs will be fully calibrated as follows: Connect the inorganic standard gas bottle to the gas sampling valve containing dual (matched ±1 percent) sample loops (1-, 3-, and 5-mL loop sizes should be available). Flow the gas through the valve at a constant and reproducible flow rate of 20 stdmL/min, measured at the sample valve outlet with a soap bubble flow meter. When the valve is sufficiently purged, actuate the valve and inject the contents of the first sample loop into the chromatograph. Simultaneously start the integrator. When the CO_2 peak has eluted in the Chromosorb 102 column, switch to the second loop connected to the Molecular Sieve 13X column and obtain the remaining peaks. The retention times and peak areas of replicate standards must agree to within 5 percent relative standard deviation. The inorganic standard gas mixture will be injected and analyzed at the beginning and end of each day. The retention times and responses of each component must agree with the initial site calibration data to within ±10 percent.

The analysis of an actual sample proceeds as follows:

a. Set up chromatograph, recorder, and integrator according to manufacturers' manuals, calibrate, and confirm operating parameters (list these on each chromatogram).

b. Conditions

Carrier flow rate: 30 ±2 mL/min nitrogen
Bridge current: 100 mA
Detector temperature: 100° C
Oven temperature: 45° C
Attenuator: as required
Recorder: 1 mV full scale, 1 in./min
Integrator: as required

c. Label the recorder chart with sample number, date, and operating parameters.

d. Connect the gas sampling container to the gas sampling valve. Purge the sample loops with the sample. Inject the sample.

e. Simultaneously start the integrator and recorder.

f. When the analysis is finished, give the chromatogram and integrator output to the data analyst.

The required data for these analyses are on the data sheet. Data reduction is effected as follows:

a. Components (CO, CO_2, O_2, N_2) are identified by retention time comparison with the standard chromatograms (flow rate reproducibility is critical).

b. Divide the areas found in the sample chromatogram by the appropriate slope and obtain the concentration of each component in mg/m^3.

Periodically, the gas sampling valve should be checked to determine if it is contributing contamination to the analysis of samples. Pass dried and filtered reactor grade helium carrier through the sample loops; then inject their contents and analyze as if it were a sample. If significant peaks are noted, the valve should be cleaned per the manufacturer's instructions.

Calibration of the gas chromatograph is performed as follows:

a. Calculate the average and standard deviation of the retention times and responses from the chromatograms of the standard gas mixtures.

b. Plot responses (μV·sec) as ordinates versus component concentrations (mg/m^3) as abscissa. Draw in the curves. Perform least squares linear regressions for each component, and obtain the slopes (μV·sec·m^3/mg).

3.6.3 Analysis of Sulfur Compounds

In the field, sulfur compounds are analyzed by gas chromatography using flame photometric or thermal conductivity detectors. The procedure and conditions of operation are listed in Table 7 for a dual flame FPD and a thermal conductivity detector. Use the manufacturer's recommended conditions for air, hydrogen flow rates, and thermal conductivity filament current. It is important to note that in the analysis of sulfur compounds, the sample must not come in contact with anything but Teflon or glass until it reaches the detectors.

If the sample contains high concentrations of hydrogen sulfide (>200 ppm), then the sample should be analyzed by gas chromatography with a thermal conductivity detector. At concentration levels of about 100 ppm and lower, a flame photometric detector with a 394-nm filter is very suitable for sulfur compounds analysis because of its specificity and sensitivity.

The procedure for the analysis of sulfur compounds is as follows: The GC injection system including the Teflon loop is evacuated to 1 mmHg using the pump. A small amount of sample from the containers is then introduced and the system reevacuated for adequate flushing. A known amount of standard sulfur gases is introduced into the sample loop and injected onto the GC columns specified for the respective gases in Table 7. The areas of the eluting peaks are printed by the digital integrator or calculated manually and calibration plots of area versus concentrations for each individual gas should be drawn. The unknown sample is then injected, the eluting peaks are identified by their retention times, and the respective concentrations are noted from the calibration plots.

3.6.4 Organic Species (bp <100° C) Analytical Methodology

Materials with boiling points below 100° C require an onsite gas chromatographic analysis of a collected sample. Two separate GC procedures are required in order to allow resolution of the very volatile organics while eluting the higher boiling gases in a reasonable period of time. The GC systems will primarily be separating materials on the basis of boiling point ranges, although the separations will also be influenced by polarity in some cases. A gas chromatograph with a flame ionization detector is needed.

The conditions recommended for these analyses are specified in Table 7. Slight modifications in temperature and duration of the isothermal hold periods and/or rate of temperature increase may be necessary to accommodate variations in individual column performance.

The GC system should be calibrated for quantitative analysis with a normal hydrocarbon mixture. The sample analysis procedure is to connect the glass gas containers to the sampling valve and draw the gas through the valve and loop. When the sample valve is sufficiently purged, actuate the valve and inject the contents of the sample loop into the chromatograph. Simultaneously start the integrator and temperature programmer. Obtain the chromatograms and the integrator output. Retention times and responses shall agree to within 5 percent relative standard deviation. Assumption of uniform flame ionization detector (FID) response for varying compound classes is acceptable in Level 1 analysis.

The C_1-C_7 standard gas mixture should be used to calibrate the field GC procedures and should be analyzed at the start of each day. A retention time vs. boiling point calibration curve is prepared for each compound in the standard manner. The Level 1 boiling point ranges and the hydrocarbons falling in each range are given in Table 8.

Since the chromatogram peaks for Level 1 samples will usually represent mixtures of materials present in a certain boiling range rather than pure individual compounds, it is recommended that the chromatographic data be reported on the Organic Compounds form shown in Appendix A.

It is important to recognize that in many, if not most, cases, the species present will not be identical to those used for calibration of the onsite procedure. The required data for sampling, calibration, and analysis are summarized in the data sheets. Any subsequent data interpretations must use sensitive criteria (MATE value of the worst case compound unless that compound is ruled out, in which case the next lowest MATE value would be assumed, etc.) in that boiling range; not the normal hydrocarbon MATE value.

TABLE 8. LEVEL 1 BOILING POINT RANGES

Level 1 designation	bp range (°C)	Hydrocarbon	bp (°C)
GC1	-160 to -100	Methane, C_1	-161
GC2	-100 to - 50	Ethane, C_2	- 88
GC3	- 50 to 0	Propane, C_3	- 42
GC4	0 to 30	Butane, C_4	0
GC5	30 to 60	Pentane, C_5	36
GC6	60 to 90	Hexane, C_6	69
GC7	90 to 100	Heptane, C_7	96

CHAPTER 4

SAMPLING OF PARTICULATE AND VAPOR STREAMS

4.1 INTRODUCTION

Stationary source particulate matter sampling and analysis have been restricted to streams of high mass loading until recently because the flow rates through sampling equipment had not been high enough to collect an adequate amount of material in a reasonable length of time (refs. 7, 25, 26). Because of this restriction, the development and application of control technology, which requires effluent information on four particulate size ranges, has been hampered. It has also limited health effects studies, which require information on the distribution and composition of respirable and nonrespirable particulate size classes, the presence of volatile organic compounds, and the presence of trace elements to be complete. To correct this situation, EPA (IERL-RTP) has developed and specified the use of the Source Assessment Sampling System (SASS)* for the collection of particulate samples and volatile matter from ducted emissions (Figure 8).

The SASS train consists of a stainless steel probe that connects to three cyclones and a filter in an oven module, a gas treatment section, and an impinger series (see Figure 8). Size fractionation is accomplished in the cyclone portion of the SASS train, which incorporates the three cyclones in series to provide large collection capacities for particulate matter nominally size-classified into three ranges: (a) >10 μm, (b) 3 μm to 10 μm, and (c) 1 μm to 3 μm. By means of a standard 142-mm or 230-mm filter, a fourth cut, <1 μm, is also obtained. The gas treatment system follows the oven unit and is composed of four primary components: the gas cooler, the sorbent trap, the aqueous condensate collector, and a temperature controller. Volatile organic material is collected in a cartridge or "trap" containing a

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*Manufactured by Aerotherm Corporation, 485 Clyde Avenue, Mountain View, CA 94042, (415)964-3200.

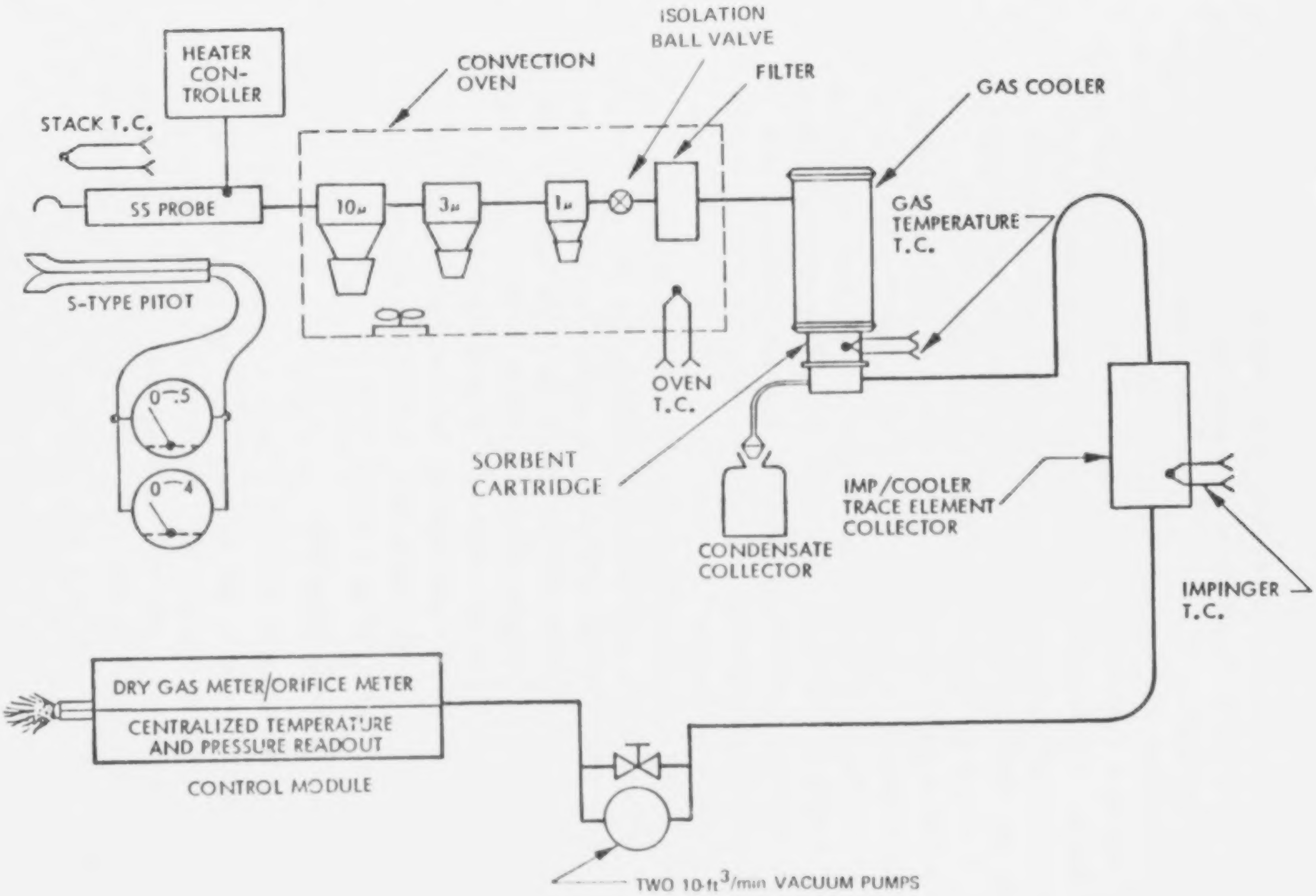

ISOLATION
BALL VALVE
HEATER
CON-
TROLLER
CONVECTION
OVEN
FILTER
GAS COOLER
STACK T.C.
SS PROBE
10μ
3μ
1μ
GAS
TEMPERATURE
T.C.
S-TYPE PITOT
0–.5
0–4
OVEN
T.C.
SORBENT
CARTRIDGE
IMP/COOLER
TRACE ELEMENT
COLLECTOR
CONDENSATE
COLLECTOR
IMPINGER
T.C.
DRY GAS METER/ORIFICE METER
CENTRALIZED TEMPERATURE
AND PRESSURE READOUT
CONTROL MODULE
TWO 10-ft³/min VACUUM PUMPS

Figure 8. Source assessment sampling train schematic.

sorbent, which is designated to be XAD-2, a microreticular resin with the capability of adsorbing a broad range of organic species. Volatile inorganic elements are collected in a series of impingers that follow the condenser and sorbent system. The last impinger in the series contains silica gel for moisture removal. Trapping of some inorganic species also may occur in the sorbent module. The pumping capacity is supplied by two 10-ft^3/min, high-volume vacuum pumps, while required pressure, temperature, power, and flow conditions are regulated through a main controller. At least 60 A of power at 110 V is needed for operating the sampling equipment.

The gross volume of sample needed in order to perform the required analyses as presented in Chapter 1 (Table 2) is 30 dsm^3. This sample must be taken with a flow rate of 0.184 sm^3/min (6.5 sft^3/min) at the cyclones, which will result in a flow rate of about 0.113 dsm^3/min (4 $dsft^3$/min) at the dry gas meter. The PMB has developed an additional series of sampling guidelines criteria for acquiring the required quantity of sample during each run. These criteria are:

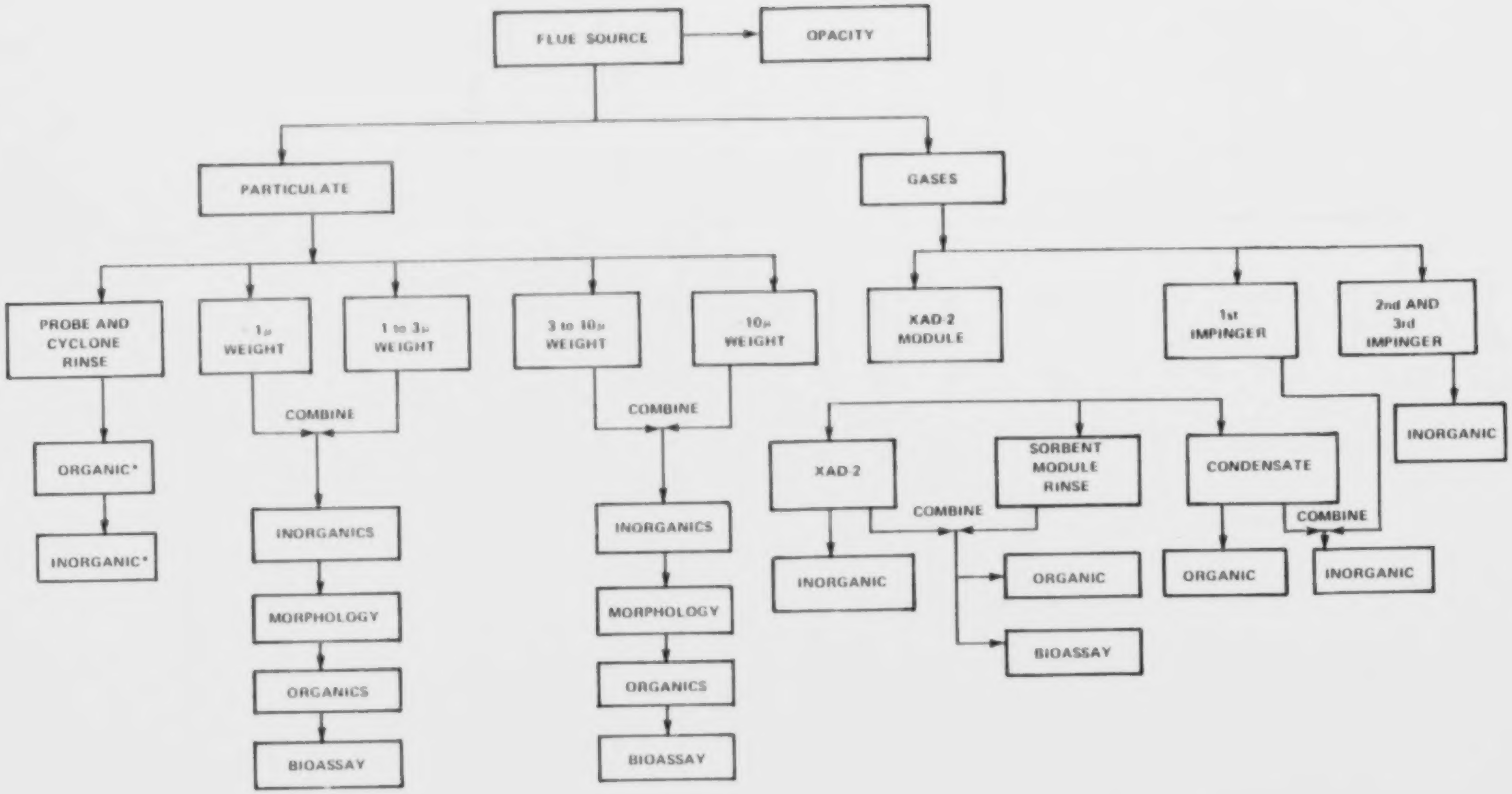
a. At least one full process cycle and 30 dsm^3 (1,060 $dsft^3$) of the process effluent are to be sampled during each run.

b. In the event that the process is not cyclic in nature, the 30 dsm^3 figure must still be satisfied over a period of time conducive to obtaining a sample representative of process conditions. A sample duration of 5 h has satisfied this requirement in the past.

Schematics outlining flue gas sampling and analysis are shown in Figures 9 and 10. Details of the sample handling and transfer procedures are presented in a later section of this chapter.

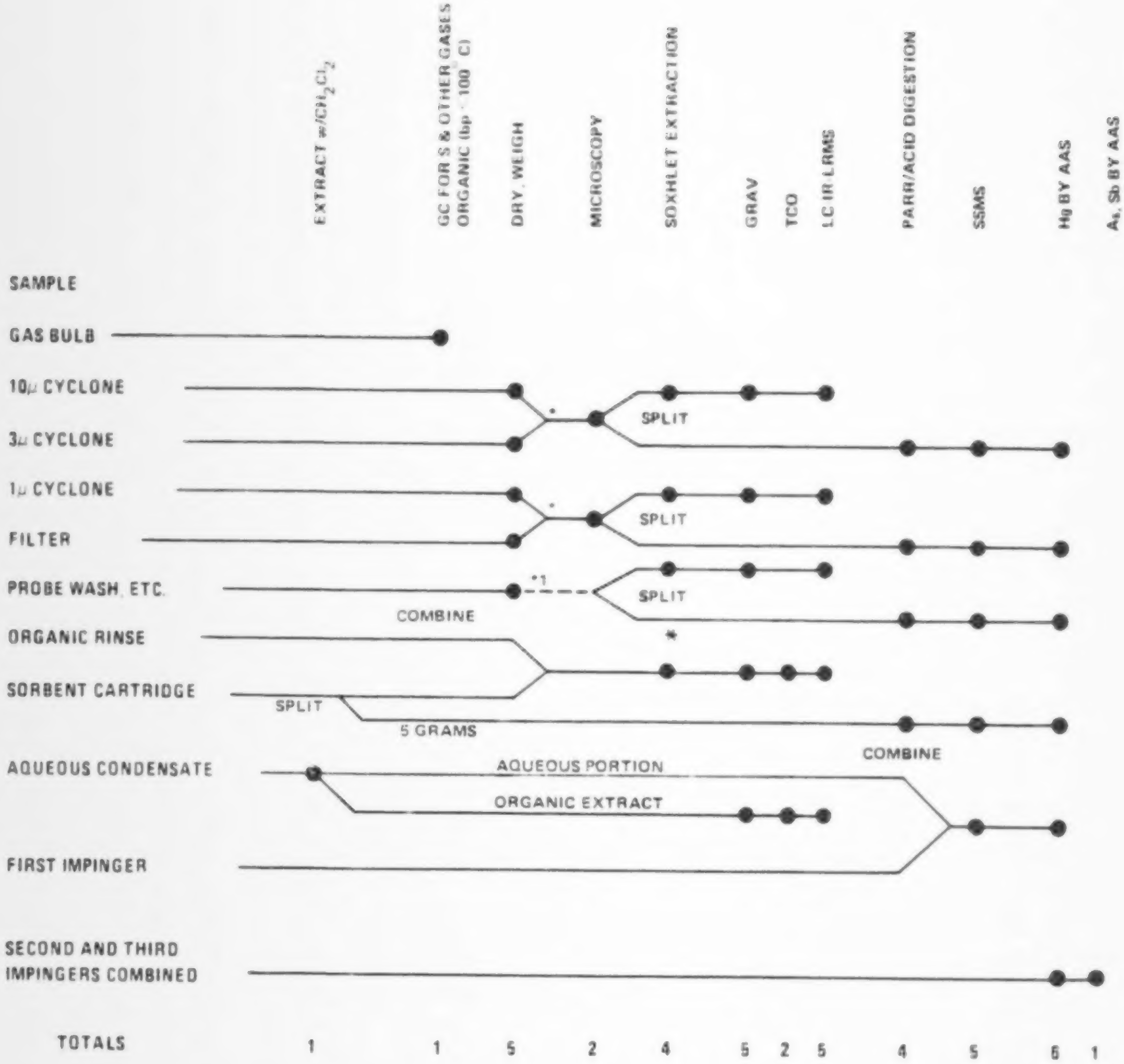
4.2 EQUIPMENT AND PERSONNEL REQUIREMENTS

The apparatus and reagents required to perform a source assessment sampling are shown in Table 9. The personnel requirements are related to the magnitude of the sampling task, with three as the minimum number of people per SASS system. A relatively linear correlation may be made between time requirements and number of SASS teams deployed in a given sampling task (refs. 6, 25, 27, 28).


FLUE SOURCE
OPACITY
PARTICULATE
GASES
PROBE AND CYCLONE RINSE
1μ WEIGHT
1 to 3μ WEIGHT
3 to 10μ WEIGHT
10μ WEIGHT
XAD 2 MODULE
1st IMPINGER
2nd AND 3rd IMPINGER
COMBINE
COMBINE
XAD 2
SORBENT MODULE RINSE
CONDENSATE
INORGANIC
ORGANIC*
INORGANIC*
INORGANICS
MORPHOLOGY
ORGANICS
BIOASSAY
INORGANICS
MORPHOLOGY
ORGANICS
BIOASSAY
COMBINE
COMBINE
INORGANIC
ORGANIC
BIOASSAY
ORGANIC
INORGANIC

*Analysis when 10 percent of the total particulate catch

Figure 9. Flue gas sampling flow diagram.


EXTRACT w/CH$_2$Cl$_2$
GC FOR S & OTHER GASES ORGANIC (bp < 100° C)
DRY, WEIGH
MICROSCOPY
SOXHLET EXTRACTION
GRAV
TCO
LC IR LRMS
PARR/ACID DIGESTION
SSMS
Hg BY AAS
As, Sb BY AAS
SAMPLE
GAS BULB
10µ CYCLONE
3µ CYCLONE
SPLIT
1µ CYCLONE
FILTER
SPLIT
PROBE WASH, ETC.
*1
SPLIT
COMBINE
ORGANIC RINSE
*
SORBENT CARTRIDGE
SPLIT
5 GRAMS
COMBINE
AQUEOUS CONDENSATE
AQUEOUS PORTION
ORGANIC EXTRACT
FIRST IMPINGER
SECOND AND THIRD IMPINGERS COMBINED
TOTALS
1
1
5
2
4
5
2
5
4
5
6
1

* If required, sample should be set aside for biological analysis at this point.

[1] This step is required to define the total mass of particulate catch. If the sample exceeds 10% of the total cyclone and filter sample weight, proceed to analysis. If the sample is less than 10% of the catch, hold in reserve.

Figure 10. Flue gas analysis requirements.

TABLE 9. APPARATUS AND REAGENTS FOR A SASS RUN

Item	Apparatus quantity
4-liter glass or high density polyethylene containers to be used in cleaning operations	Assume 5 per SASS run
Nylon brushes	Assume 5 per SASS run
150 x 25 mm diameter glass test tubes with caps	Assume 3 per SASS run
Linear high density polyethylene wide-mouth containers for particulate	Assume 10 per SASS run
Amber glass containers for organic solutions, 500-mL capacity	Assume 5 per SASS run
Linear high density polyethylene containers for impinger solutions, 1-L capacity	Assume 5 per SASS run
Linear high density polyethylene containers, 0.5-L capacity	Assume 2 per SASS run
Reagents	Item
Aqueous nitric acid (15%)	ACS REAGENT GRADE
Distilled water	OR BETTER QUALITY
Methylene chloride (distilled in glass)	UNLESS SPECIFIED
Silica gel (desiccant)	
Hydrogen peroxide	
Silver nitrate	
Ammonium persulfate	
Methanol (distilled in glass)	
Miscellaneous	Item
XAD-2 resin (special instructions for cleaning the XAD-2 resin are provided in Appendix B)	Assume 150 g per SASS run
Reeve Angel 934 AH filter	Assume 3 per SASS run

The acquisition of a Level 1 sample using a SASS train generally requires two and, in some cases, three persons for equipment assembly and disassembly. After assembly, the train requires one full-time and one half-time person for operation. The remaining manpower is then available for other onsite efforts. Each SASS train run will consist of approximately a 5-h period (specific sample acquisition criteria are described later in this chapter). The number of required personnel for this function will not increase regardless of the number of sample sites, provided that a sufficient time allotment exists within the sampling task to allow for consecutive sampling. Manpower projections can thus be determined by considering the number of SASS particulate samples required to characterize the location in question, the time required for the acquisition of each sample, and the number of personnel and/or samplers available for the task.

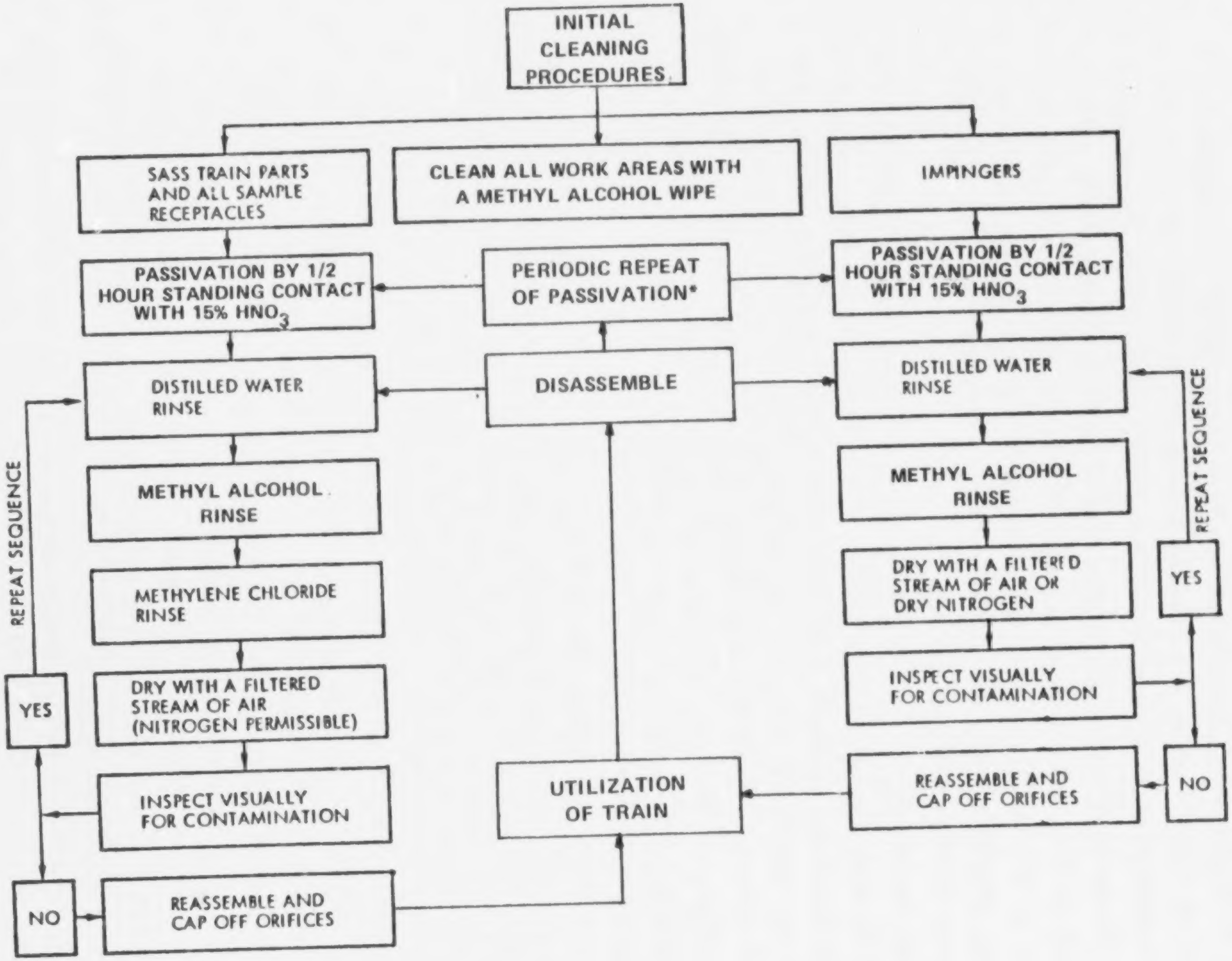
4.3 EQUIPMENT PREPARATION FOR SAMPLE COLLECTION

The following sections discuss the equipment preparation required for the SASS train, including procedures for cleaning the train components and sample containers. For further information on the device see the Operating and Service Manual Source Assessment Sampling System (ref. 29). The SASS train schematic and other parts of the train are shown in Figure 8.

4.3.1 Precleaning Procedures for the SASS Train and Sample Containers (refs. 7, 8, 25, 30, 31)

Since the SASS train is the most complex sampling unit discussed in this manual, a generalized cleaning procedure is presented in Figure 11. Two primary cleaning methodologies are required. The first methodology, described in this section, concerns the technique involved in producing biologically inert surfaces throughout the SASS train. The second methodology, described in Section 4.5, Sample Handling and Shipment, presents the techniques required for cleaning or removing sample from various parts of the train after the run.

The first stage in preparing a new sampling train and new sample containers for sample collection is prepassivation with a nitric acid solution. All metal and glass surfaces in the sampling train that come in contact with


INITIAL CLEANING PROCEDURES
SASS TRAIN PARTS AND ALL SAMPLE RECEPTACLES
CLEAN ALL WORK AREAS WITH A METHYL ALCOHOL WIPE
IMPINGERS
PASSIVATION BY 1/2 HOUR STANDING CONTACT WITH 15% HNO$_3$
PERIODIC REPEAT OF PASSIVATION*
PASSIVATION BY 1/2 HOUR STANDING CONTACT WITH 15% HNO$_3$
DISTILLED WATER RINSE
DISASSEMBLE
DISTILLED WATER RINSE
METHYL ALCOHOL RINSE
METHYL ALCOHOL RINSE
METHYLENE CHLORIDE RINSE
DRY WITH A FILTERED STREAM OF AIR OR DRY NITROGEN
DRY WITH A FILTERED STREAM OF AIR (NITROGEN PERMISSIBLE)
INSPECT VISUALLY FOR CONTAMINATION
INSPECT VISUALLY FOR CONTAMINATION
YES
REPEAT SEQUENCE
YES
REPEAT SEQUENCE
NO
REASSEMBLE AND CAP OFF ORIFICES
UTILIZATION OF TRAIN
NO
REASSEMBLE AND CAP OFF ORIFICES

*Refer to text for passivation time schedule.

Figure 11. SASS cleaning procedures.

the sample will be prepassivated by a 30-min standing contact with 15 percent (v/v) aqueous nitric acid. Use a stiff nylon brush or hard Teflon scraper to aid in cleaning encrusted materials from the surfaces if necessary. Agitate the parts initially to remove trapped air bubbles. Rinse in a second solution of 15 percent (v/v) HNO_3, then rinse with distilled water. Next, rerinse by spraying thoroughly with alcohol (taking care to cover all surfaces) or dip in alcohol and agitate for 10 s. Finally, dry with purified air or nitrogen. If the impingers are to be used immediately after cleaning, they should be thoroughly dried or rerinsed with distilled water to prevent foaming when the peroxide is added.

Passivation should be carried out initially (as stated above) and then every 6 mo when the frequency of tests is one per month or less, every 3 mo when the frequency of tests is between one per week and one per month, and monthly for testing in excess of one per week. If the tests are more frequent or of longer duration, passivation should be conducted more frequently. If corrosion has occurred, the corrosion should be removed and the passivation repeated. The passivation and rinse solutions should be replaced after every fourth use or should be discarded weekly.

Two separate approaches are used for subsequent cleanings of SASS train components and organic sample receptacles and for bottles holding impinger solutions. The components and receptacles are cleaned in three successive stages using a different solvent in each stage. The solvents used are distilled water, methanol, and methylene chloride, in the order listed. This procedure removes all extraneous particulate matter and produces a clean, dry surface. As each part is treated with the final solvent (methylene chloride), it is purged dry in a filtered stream of air or dry nitrogen and inspected thoroughly for any sign of contaminating residue, scale, rust, etc. A contaminated train component may not be used in a sampling run. All equipment treated in the above fashion must be placed in a clean area to await the next test. The bottles holding the impinger solutions are cleaned with distilled water.

The field area in which these cleaning operations are performed must be as clean as possible under existing field conditions. An enclosed space is required in which reasonable precaution has been taken to remove spurious dust, dirt, or particulate contaminants. Reasonable precaution is intended to mean that the area has been swept clean, doors or significant draft-inducing sources have been closed, and all work bench areas have been wiped down with methanol.

4.3.2 Apparatus Checkout

The following tasks should be performed in the home base laboratory prior to shipment:

a. Assemble all components required for the complete system.
b. Clean components in accordance with the procedures described in Section 4.3.1.
c. Obtain a sufficient quantity of solvents to maintain adequate reserves during the elapsed time in the field.
d. Obtain a tank of purified dry nitrogen or clean compressed air.
e. Accumulate an inventory of Swagelok fittings (in triplicate) for each SASS train.
f. Examine all SASS train parts closely for defects that might induce down-time problems in the field.
g. Leak-check the entire system.

Besides the cleaning procedures, leak-checking the train prior to field use is one of the most important pretest tasks to be performed. This procedure can save hours of time in the field. The leak-checking procedure involves assembling the entire train, sealing the probe tip, opening the isolation ball valve, turning on the pumping system, and observing flow meter gauges for the existence of any appreciable flow. Evacuate the train to 127 mmHg (5 inHg). The allowable leak rate for the SASS train is 0.0014 m^3/min (0.05 ft^3/min) at this pressure. Close the isolation ball valve and leak check the remainder of the train at 508 mmHg (20 inHg). The leak rate should again be less than 0.0014 m^3/min (0.05 ft^3/min). If this criterion is not easily achievable using Teflon gaskets in the system, Viton A gasket substitution may facilitate meeting this standard. The instructions accompanying the train will present in detail the steps involved in leak-checking the system.

4.4 SASS TRAIN SAMPLING PROCEDURE (refs. 8, 17, 32-34)

A Level 1 SASS sample is acquired at a point of average velocity near the center of the duct (the average velocity being determined by a velocity traverse). The sample is withdrawn at a constant flow rate using a nozzle that is specifically selected for near isokinetic conditions when the test is initiated.

The steps involved in using the train to acquire this sample are described in detail in the manuals provided with the SASS train. An outline of the procedure follows:

I. Test Site
    A. Prepare sampling port on duct, flue, or stack.
    B. Secure electrical power.
II. SASS Train Assembly
    A. Attach probe to oven.
    B. Assemble the three cyclones. (Note that to achieve the proper size fractionation, the vortex breakers for the ">10 μm" and for the "10- to 3-μm" cyclones should not be used. The vortex breaker for the "3- to 1-μm" cyclone should, however, be included in the train assembly.) Fit the filter into the filter holder and place the combined components in the oven.
    C. Connect large cyclone to probe.
    D. Assemble impinger train.
        1. Place heat exchanger tubing in impinger case.
        2. Fill impinger bottles with the reagents listed in Table 10.
        3. Place bottles in tray in impinger case, cap bottles, and make appropriate connections.
        4. Connect recirculation pump (for cooling gas) and fill impinger case with ice and water.
    E. Connect oven outlet (i.e., filter housing outlet) to gas cooler/gas adsorbent/condensate reservoir assembly.
    F. Connect gas cooler/gas adsorbent/condensate reservoir assembly to first impinger bottle.
    G. Connect gas cooling systems.

H. Connect gas condensate collector bottle to gas cooler/gas adsorbent/condensate reservoir assembly.

I. Connect vacuum pumps in parallel to fourth impinger outlet.

J. Connect all temperature sensors and power lines to control unit.

III. Checkout and Inspection

A. Run gas flow leak check.

B. Check temperature indicators with all thermocouples at ambient temperature.

C. Activate gas cooling systems. IT IS EXTREMELY IMPORTANT THAT THE XAD-2 RESIN NEVER BE ALLOWED TO RISE IN TEMPERATURE ABOVE 50° C, AS DECOMPOSITION WILL OCCUR. This decomposition will result in high TCO blanks.

D. Heat oven and probe to 204° C (400° F).

E. Note operation of vacuum pumps and gas meter.

F. Inspect pitot tube; also, compare results of volume measured with orifice meter and dry gas meter. Calibrate each as necessary.

IV. Operation

A. Measure stack temperature, moisture content, and velocity profile.

B. Calculate size of probe nozzle needed for isokinetic sampling and select and attach appropriate size nozzle. The effluent water vapor content must be considered when choosing the proper nozzle size.

C. Calculate train gauge reading to achieve train flow rate of 0.113 sm^3/min (4.0 sft^3/min). (This flow rate is necessary for proper operation of the cyclones.)

D. Install probe in stream at point of average stream velocity and turn on vacuum pumps; adjust train flow rate to 0.113 sm^3/min.

E. Collect sample. Monitor all temperatures and flow rates, and adjust as necessary.

F. Regularly drain condensate from condensate reservoir.

V. Shutdown
   A. Close valves at pumps.
   B. Let vacuum return to zero.
   C. Turn off pumps.
   D. Switch off main power.

For the accuracy requirements of Level 1, the duct flow rate is allowed to vary from -30 to +50 percent of the specified isokinetic rate. Conditions existing outside of the above-specified margin must result in SASS train shutdown for an inspection and correction; for example, changing the probe nozzle. The cause of the deviation from isokinetic conditions frequently may be traced to a continuous high grain-loading density, an increase or decrease in gas velocity, or a buildup of particulates leading to failure of the pump to pull at the rate required to meet particulate matter collection requirements.

Three possible situations occurring within the SASS train will manifest pressure variations outside of the acceptable margin. They are clogging of the probe nozzle, clogging of the filter, and saturation of the silica gel. The solution in these cases requires SASS train shutdown and probe nozzle cleaning or filter or silica gel replacement.

TABLE 10. SASS TRAIN IMPINGER SYSTEM REAGENTS

Impinger	Reagents	Quantity	Purpose
#1	30% H_2O_2	500 mL	Trap reducing gases such as SO_2 to prevent depletion of oxidative capacity of trace element collecting impingers 2 and 3.
#2	0.2 M $(NH_4)_2S_2O_8$ +0.02 M $AgNO_3$	500 mL	Collection of volatile trace elements by oxidative dissolution.
#3	0.2 M $(NH_4)_2$ S_2O_8 +0.02 M $AgNO_3$	500 mL	Collection of volatile trace elements by oxidative dissolution.
#4	Silica gel	750 g	Prevent moisture from reaching pumps.

Replacement of a clogged filter is a time-consuming process that could require as much as 2 h, depending on the sampling location and the possible difficulties that might be encountered in removing the housing. Once removed, the housing should be carried intact to a clean area for filter removal. A second, preloaded filter housing should be available for use when the first housing is removed for unloading, cleaning, and reloading. Check this assembled replacement filter assembly for leaks before placing it in service, then make a final check of the pressure drop of the whole SASS system when the unit is again reassembled. The 1-µm cyclone reservoir should be checked for remaining capacity whenever the filter is replaced. Take care not to contaminate the contents during this inspection. For a standard test, 30 dsm^3 of gas must have been sampled.

4.5 SAMPLE HANDLING AND SHIPMENT (refs. 7, 8, 30, 33, 35)

The procedures used in transferring acquired sample from various portions of the SASS train are complex. Therefore, a modular approach will be used to expedite the explanation of the procedures involved in sample transfer and handling. For this reason, the SASS train is considered in terms of the following sections:

a. Nozzle and probe,
b. Cyclone system interconnect tubing,
c. Cyclones,
d. XAD-2 module, and
e. Impingers.

At the conclusion of the sampling run, the train is disassembled and transported to the mobile lab unit or prepared work area as follows:

a. Open the cyclone oven to expedite cooling, disconnect the probe, and cap off both ends.
b. Disconnect the line joining the cyclone oven to the gas adsorbent assembly at the exit side of the filter and cap off (1) the entrance to the 10-µm cyclone, (2) the filter holder exit, and (3) the entrance to the join line, which was disconnected from the filter holder exit point.
c. Disconnect the line joining the adsorbent module to the impinger system at the point where it exits the adsorbent module. Cap off

the exit of the adsorbent module and the entrance line to the impinger system.

d. Disconnect the line leaving the silica gel impinger at its exit point and cap off the impinger exit. Discard ice and water from the impinger box to facilitate carrying.

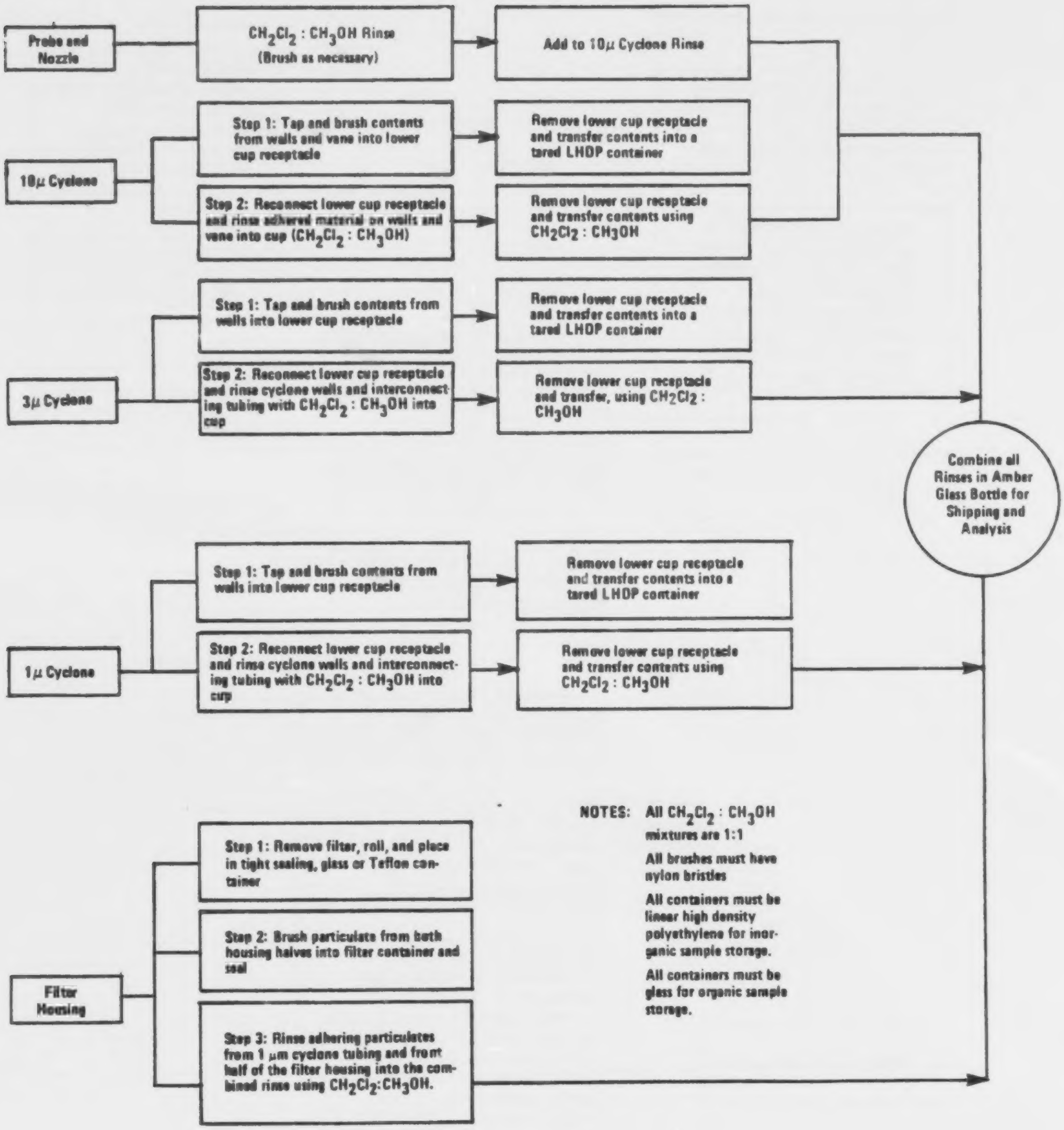
The solvent system found to be the most effective for rinse and final cleanout of adhered sample consists of a 1:1 mixture of methylene chloride (CH_2Cl_2) and methanol (CH_3OH) for the front half of the SASS train. Methylene chloride alone is to be used in the gas cooler and sorbent module rinses because methanol will interfere with the LC separation. Each step is presented in the series of flow diagrams in Figures 12, 13, and 14. It is suggested that these diagrams be placed in an easily visible location near the cleaning area as an aid to the sample transfer activity. Samples will be shipped to the laboratory in the most expeditious manner possible in order not to delay analysis unnecessarily. One special concern is the H_2O_2 solution from the first impinger. Special precautions must be taken to ship this dangerous material. Instructions for shipment are as follows:

a. Place bottle containing sample into polyethylene bag and secure with twist tie.
b. Line bottom of steel drum with 1-in. layer of vermiculite.
c. Place bottle in drum and pack around sides and over top with more vermiculite.
d. Label drum "oxidizer."
e. Corrosive and/or flammable samples cannot be packed in same drum as H_2O_2 samples.
f. Ship drum by cargo-only aircraft.

At the completion of all sample transfer activities, all SASS train components must be completely recleaned in preparation for the sampling run. This may be accomplished by following the steps outlined in Figure 11.

4.6 SASS SAMPLE ANALYSIS

The type and extent of analytical testing that can be performed on SASS sample materials is determined in large part by the quantity of the sample obtained. Table 11 presents the relative order of ranking test priorities. Inorganic analysis will be performed first on samples of limited quantity. Spark source mass spectrometry analyses may be performed on a one-time basis


Probe and Nozzle
CH_2Cl_2 : CH_3OH Rinse (Brush as necessary)
Add to 10μ Cyclone Rinse
10μ Cyclone
Step 1: Tap and brush contents from walls and vane into lower cup receptacle
Remove lower cup receptacle and transfer contents into a tared LHDP container
Step 2: Reconnect lower cup receptacle and rinse adhered material on walls and vane into cup (CH_2Cl_2 : CH_3OH)
Remove lower cup receptacle and transfer contents using CH_2Cl_2 : CH_3OH
3μ Cyclone
Step 1: Tap and brush contents from walls into lower cup receptacle
Remove lower cup receptacle and transfer contents into a tared LHDP container
Step 2: Reconnect lower cup receptacle and rinse cyclone walls and interconnecting tubing with CH_2Cl_2 : CH_3OH into cup
Remove lower cup receptacle and transfer, using CH_2Cl_2 : CH_3OH
Combine all Rinses in Amber Glass Bottle for Shipping and Analysis
1μ Cyclone
Step 1: Tap and brush contents from walls into lower cup receptacle
Remove lower cup receptacle and transfer contents into a tared LHDP container
Step 2: Reconnect lower cup receptacle and rinse cyclone walls and interconnecting tubing with CH_2Cl_2 : CH_3OH into cup
Remove lower cup receptacle and transfer contents using CH_2Cl_2 : CH_3OH
Filter Housing
Step 1: Remove filter, roll, and place in tight sealing, glass or Teflon container
Step 2: Brush particulate from both housing halves into filter container and seal
Step 3: Rinse adhering particulates from 1 μm cyclone tubing and front half of the filter housing into the combined rinse using CH_2Cl_2:CH_3OH.

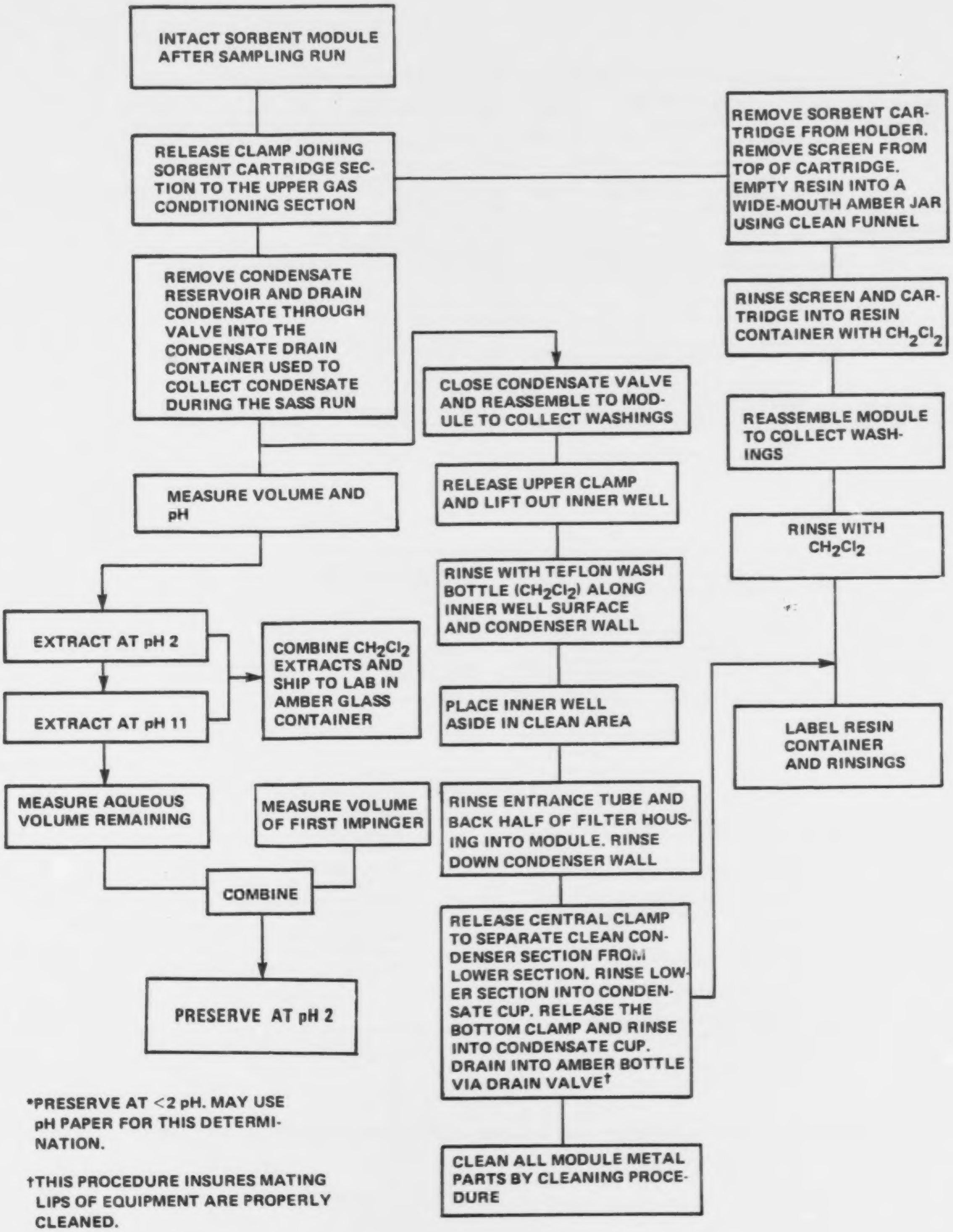
NOTES: All CH_2Cl_2 : CH_3OH mixtures are 1:1

All brushes must have nylon bristles

All containers must be linear high density polyethylene for inorganic sample storage.

All containers must be glass for organic sample storage.

Figure 12. Sample handling and transfer—nozzle, probe, cyclones, and filter.


INTACT SORBENT MODULE AFTER SAMPLING RUN
RELEASE CLAMP JOINING SORBENT CARTRIDGE SECTION TO THE UPPER GAS CONDITIONING SECTION
REMOVE SORBENT CARTRIDGE FROM HOLDER. REMOVE SCREEN FROM TOP OF CARTRIDGE. EMPTY RESIN INTO A WIDE-MOUTH AMBER JAR USING CLEAN FUNNEL
REMOVE CONDENSATE RESERVOIR AND DRAIN CONDENSATE THROUGH VALVE INTO THE CONDENSATE DRAIN CONTAINER USED TO COLLECT CONDENSATE DURING THE SASS RUN
RINSE SCREEN AND CARTRIDGE INTO RESIN CONTAINER WITH CH_2Cl_2
CLOSE CONDENSATE VALVE AND REASSEMBLE TO MODULE TO COLLECT WASHINGS
REASSEMBLE MODULE TO COLLECT WASHINGS
MEASURE VOLUME AND pH
RELEASE UPPER CLAMP AND LIFT OUT INNER WELL
RINSE WITH CH_2Cl_2
RINSE WITH TEFLON WASH BOTTLE (CH_2Cl_2) ALONG INNER WELL SURFACE AND CONDENSER WALL
EXTRACT AT pH 2
COMBINE CH_2Cl_2 EXTRACTS AND SHIP TO LAB IN AMBER GLASS CONTAINER
EXTRACT AT pH 11
PLACE INNER WELL ASIDE IN CLEAN AREA
LABEL RESIN CONTAINER AND RINSINGS
MEASURE AQUEOUS VOLUME REMAINING
MEASURE VOLUME OF FIRST IMPINGER
RINSE ENTRANCE TUBE AND BACK HALF OF FILTER HOUSING INTO MODULE. RINSE DOWN CONDENSER WALL
COMBINE
RELEASE CENTRAL CLAMP TO SEPARATE CLEAN CONDENSER SECTION FROM LOWER SECTION. RINSE LOWER SECTION INTO CONDENSATE CUP. RELEASE THE BOTTOM CLAMP AND RINSE INTO CONDENSATE CUP. DRAIN INTO AMBER BOTTLE VIA DRAIN VALVE†
PRESERVE AT pH 2
CLEAN ALL MODULE METAL PARTS BY CLEANING PROCEDURE

*PRESERVE AT <2 pH. MAY USE pH PAPER FOR THIS DETERMINATION.

†THIS PROCEDURE INSURES MATING LIPS OF EQUIPMENT ARE PROPERLY CLEANED.

Figure 13. Sample handling and transfer—XAD-2 module.

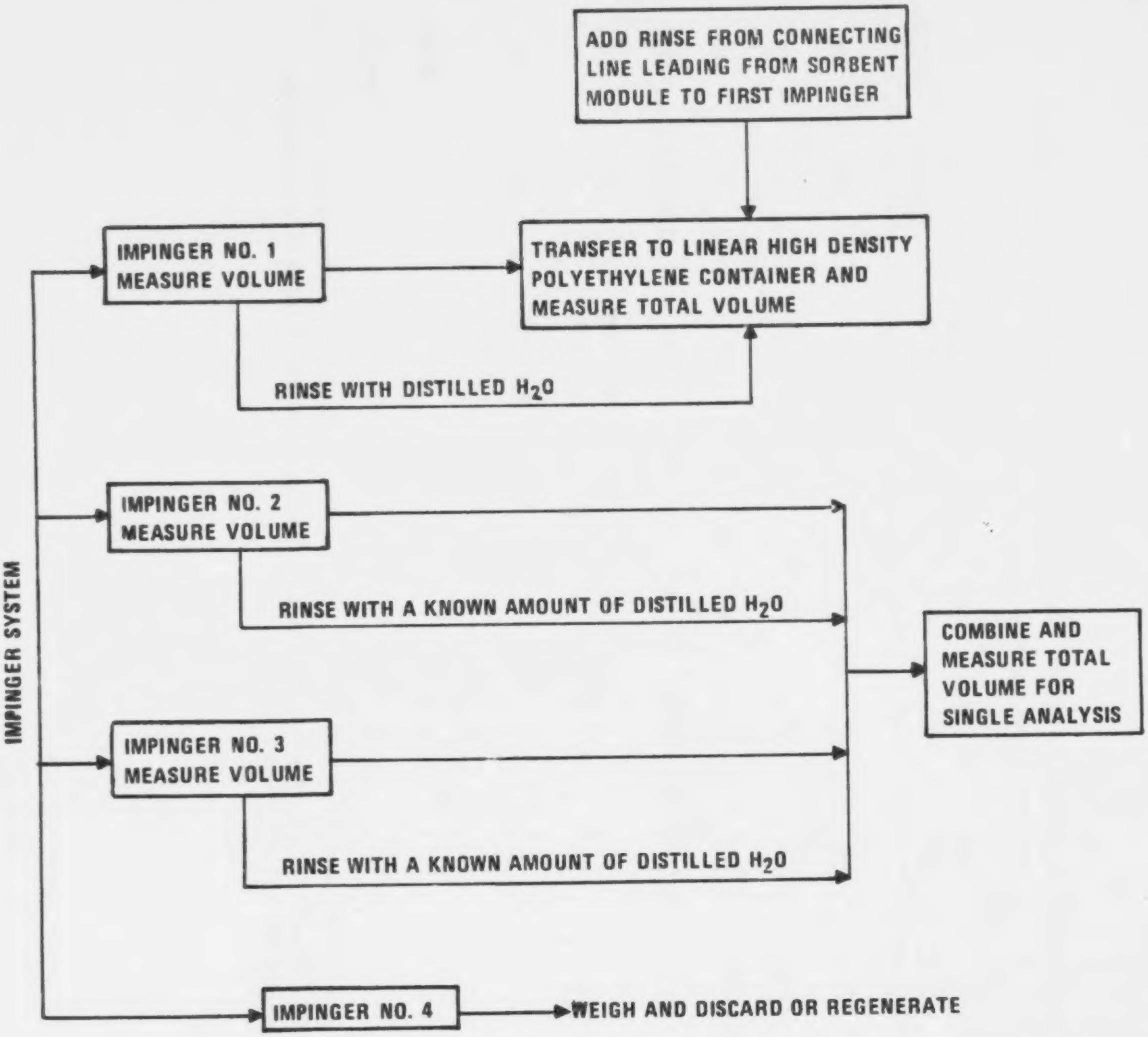

ADD RINSE FROM CONNECTING LINE LEADING FROM SORBENT MODULE TO FIRST IMPINGER
IMPINGER NO. 1 MEASURE VOLUME
TRANSFER TO LINEAR HIGH DENSITY POLYETHYLENE CONTAINER AND MEASURE TOTAL VOLUME
RINSE WITH DISTILLED H2O
IMPINGER SYSTEM
IMPINGER NO. 2 MEASURE VOLUME
RINSE WITH A KNOWN AMOUNT OF DISTILLED H2O
COMBINE AND MEASURE TOTAL VOLUME FOR SINGLE ANALYSIS
IMPINGER NO. 3 MEASURE VOLUME
RINSE WITH A KNOWN AMOUNT OF DISTILLED H2O
IMPINGER NO. 4
WEIGH AND DISCARD OR REGENERATE

Figure 14. Sample handling and transfer—impingers.

TABLE 11. SUGGESTED SASS SAMPLE DISTRIBUTION BASED ON TOTAL SAMPLE AVAILABLE*

(total sample available, mg)

Analysis	<50	>50 <70	>70 <80	>80 <180	>180 <380	>380 <480	>480 <1,680	>1,680 <2,910	>2,910 <27,960	>27,960
SSMS	All	50	50	50	50	50	50	50	100	100
Hg			20	20	20	20	20	20-50	50	50
Microscopy		Remainder	Remainder	10	10	10	10	10	10	10
Organic				Remainder	100-299	100-199	100-1,300	1,300	1,300-26,300	1,300
Ames						200	200	200 + 40% to 1,000	1,000	1,000
Cytotoxicity (RAM)							100	100 + 20% to 500	500	500
Whole Animal										25,000
Reserve										Remainder

*Example: The quantity of material collected in the SASS cyclones may not be greater than a few hundred milligrams even when the 10-μm and 3-μm particulates are combined. The same is often true for the filter catch and 1-μm cyclone particulate weights.

with 50 mg of sample or less. Mercury analysis may be obtained with 20 mg of material to give 1 ng/kg detection limits. Optical microscopy operations as described in Chapter 10 can be performed on less than 10 mg of sample. This priority is followed by organic analysis of 200 mg. Note that this quantity is the minimum amount of material that can be extracted and assayed in the techniques presented here. More sample material is apportioned relative to its availability. To perform the liquid chromatography separation in an effective manner, 75 to 100 mg of extracted material are needed. The next analysis in the priority scheme is the Ames assay, which requires an additional 200 mg of sample. This is followed by one of the cytotoxicity assays, which needs another 200 mg, and the soil microcosm test. The relative priority of whole animal toxicity testing is noted here although there will rarely be an additional 25 grams from SASS train catches available for this test. See the following chapters for more complete descriptions of the sample handling methods and analytical procedures for each test.

4.7 PLUME OPACITY TESTS

Plume opacity determinations shall be conducted for all sources. An acceptable test utilizes a chart that consists of a series of graduated shades of grey, varying in five equal steps from white (0) to black (5). The shades in between are represented by standard grids. In the field, a comparison is made between the stack plume and grids, and the grid number most closely resembling the plume shade is chosen and recorded. This test must be performed by a person who has at one time been certified to read plume opacity.

CHAPTER 5
FUGITIVE EMISSIONS SAMPLING

5.1 INTRODUCTION (refs. 1, 36)

Fugitive emissions are those air and water pollutants generated by activities at industrial sites that are transmitted into the ambient atmosphere or receiving water bodies without first passing through some stack, duct, pipe, or channel designed to direct or control their flow. Their generally diffuse nature and the absence of any restrictions to their dispersion preclude the use of standard stack or similar sampling methods in the quantitation of their release to the environment. These types of emissions constitute an important fraction of our total pollution problem. Therefore, a custom-designed fugitive emission sampling program must be enacted whenever there is a reasonable suspicion that fugitive emissions are being emitted from a particular industry or plant site.

This chapter describes the basic strategies that can be employed for the sampling of fugitive emissions in a Level 1 assessment effort to determine the amounts of pollutants entering the atmosphere or receiving waters. The sampling methods described are designed to provide estimates of the fugitive emissions within the accuracy limits discussed in Chapter 1.

5.2 FUGITIVE EMISSION CATEGORIES (refs. 1, 8, 36)

Fugitive emissions can be generated by almost any industrial operation from a wide variety of sources. They may or may not be visible. Airborne particulates and gases can be emitted from a number of sources in an enclosure and transmitted to the atmosphere through structural openings or vents, as with foundry casting or production-line welding operations. They can also be generated by large-scale open or semienclosed operations, such as open hearth furnaces or coke oven banks, and transmitted through roof monitors or partial hooding enclosures. A large proportion of airborne fugitive emissions is generated by sources in the open and is transmitted directly into the atmosphere, as with bulk materials storage and handling operations in coke oven operations, loading, etc..

Fugitive waterborne suspended or dissolved solids and liquids are most frequently transported to receiving bodies by stormwater runoff. Major sources of waterborne fugitive pollutants include materials from storage piles, accumulated dusts and oils from impervious areas such as paved roads or parking lots and roofs, and spills or leaks from process or handling equipment.

For Level 1 environmental assessment purposes, airborne fugitive emissions, whether particulate or gaseous, may be generally classified into two categories with regard to their method of transmittal into the atmosphere:

a. Open origin: Any open source whose gaseous and/or particulate emissions are transmitted directly into the atmosphere.

b. Semienclosed origin: Any enclosed or semienclosed source whose gaseous and/or particulate emissions are transmitted into the atmosphere through an opening other than a stack or duct.

Stormwater runoff can also be classified for Level 1 purposes into two categories with regard to its flow:

a. Overland runoff: Flow from a source directly to a receiving body on the ground surface.

b. Open channel runoff: Flow from a source into a natural or manmade channel that carries it to a receiving body.

Overland runoff will usually be found in a small area near each source where it can be isolated to estimate a specific contribution. Open channel runoff may sometimes provide specific source isolation, but will usually be found as a combination of at least two sources.

Under certain conditions, it may be necessary to sample the near-surface groundwaters for the evaluation of subsurface material transport. The project officer will make such discretionary decisions considering the probability of contamination and hazard potential relative to the costs of implementing this kind of task.

5.3 SAMPLING TECHNIQUES AND EQUIPMENT (refs. 18, 36-55)

Level 1 environmental assessment methodology requires the determination of fugitive emissions source strengths whenever there is a reasonable expectation that they exist at a specific site. The basic intent of the survey is the estimation of the fugitive emission potential of a site to determine its added impact along with that of point source emissions so that a more detailed Level 2 survey, if required, can be effectively planned and executed. For this reason, only the most generally applicable sampling techniques need to be utilized in a Level 1 survey. The techniques and equipment best suited to each of the above-defined categories of emissions are described in this section.

5.3.1 Airborne Fugitive Emissions

Open origin emissions are best sampled downwind of their source at a location where their plume or vapor is suspected to have settled to near ground level. Low molecular weight gaseous emissions are sampled using 10- to 30-L containers as described in Section 3.5.2. Particulate emissions are sampled using a high-volume sampler while vapors are collected concurrently from a side stream that is passed through a sorbent resin.

The sampler package best meeting the requirements of a Level 1 survey for airborne fugitive emissions is the Fugitive Ambient Sampling Train (FAST) sampling system (Figure 15), which was developed with the support of IERL/PMB. It is designed to provide a 500-mg particulate matter sample in an 8-h sampling period at most industrial sources. The sampling equipment is contained in a single portable unit that is connected by flexible ducting to a separate unit containing the particle sampling stream blower, organic sampling stream vacuum pump, and their electric drive motors.

The FAST system criteria include the following specifications:

a. Flow rate: Main blower capacity variable between 4.26 and 6.25 m^3/min (150 and 220 ft^3/min);
b. Flow control: Automated to maintain constant flow during the sampling period;
c. Cyclic timing: Provide preset automatic start and stop to match cyclic process emissions; and
d. Filter size: 20.3 x 25.4 cm (8 x 10 in.) Reeve Angel 934 AH filters.

The FAST sampling system consists of a single-stage cascade impactor that will collect about 90 percent of all particles larger than 15 μm, a cyclone separator with about a 50 percent collection efficiency for particles

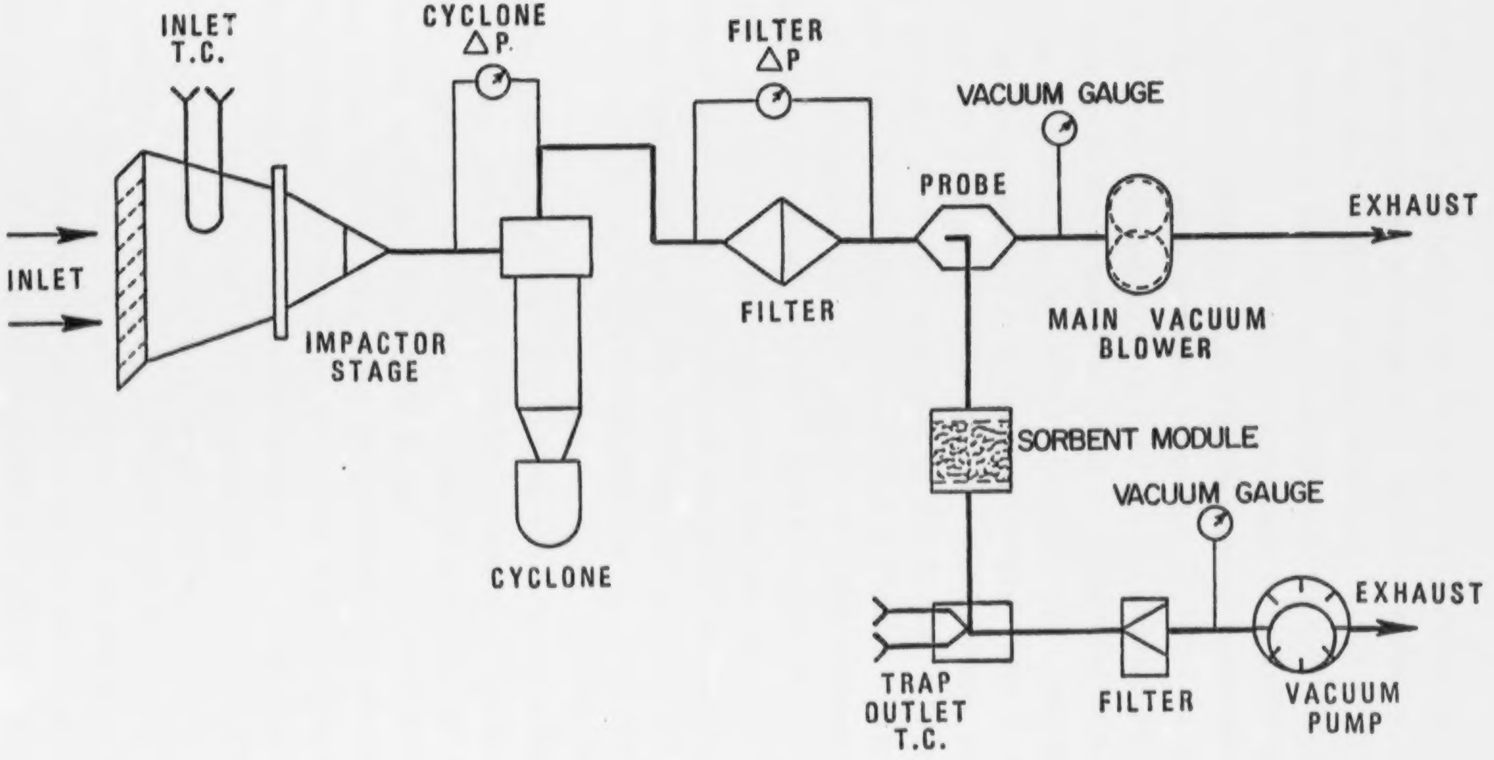

INLET
T.C.
CYCLONE
ΔP.
FILTER
ΔP
VACUUM GAUGE
INLET
PROBE
EXHAUST
IMPACTOR
STAGE
FILTER
MAIN VACUUM
BLOWER
SORBENT MODULE
CYCLONE
VACUUM GAUGE
EXHAUST
TRAP
OUTLET
T.C.
FILTER
VACUUM
PUMP

Figure 15. Fugitive Air Sampling Train components.

larger than 3 μm, and a glass fiber filter to collect the particles still entrained in the sampling stream. The particle sampling stream flow rate is 5.2 m^3/min (185 ft^3/min). A 0.14-m^3/min (5-ft^3/min) side stream is taken from the particle-free air downstream of the filter and drawn through a sorbent bed of XAD-2 to collect organic species.

As an alternative to the FAST system, a modified conventional high-volume sampler utilizing a high-speed vacuum-cleaner-type blower could theoretically be constructed for this data collection (see Figure 16). This sampler should be redesigned to approximate the performance specifications of the FAST system. This will help insure the collection of particulate and vapor samples of sufficient size to permit a reasonable estimation of their classification, concentration, and probable import to biological systems. Only the Reeve Angel 934 AH may be used as a filter for the FAST or modified high-volume system. Sampling must be interrupted to change filters whenever there is a 10 percent reduction in flow from the design criteria.

Semienclosed origin emissions, characterized by their definable plume, are best sampled using the SASS train described in Chapter 4. The train should be inserted into the plume as close to the source as possible and the sampling performed at the maximum flow rate with the largest available nozzle. Gaseous emissions are sampled using 10- to 30-L containers as previously described.

Site source emissions can generally be most effectively sampled using the upwind/downwind technique. This technique utilizes integrated sampling for gases and high-volume packages for particulates and organics to determine the background concentrations upwind of the site and total particulate or organic concentrations (including the background and any point source contributions) downwind of the site. The total fugitive emissions from the site are then calculated by subtracting the measured background and point source concentrations from the measured total pollutants. In most situations, a single upwind sampler located at the site boundary is sufficient to determine the background concentrations of substances of interest. A network of two or more samplers is usually required downwind of the site to insure accounting for variations in downwind concentration.

Measurements of local wind speed and direction and ambient temperature are also required at each source location during the sampling period. These

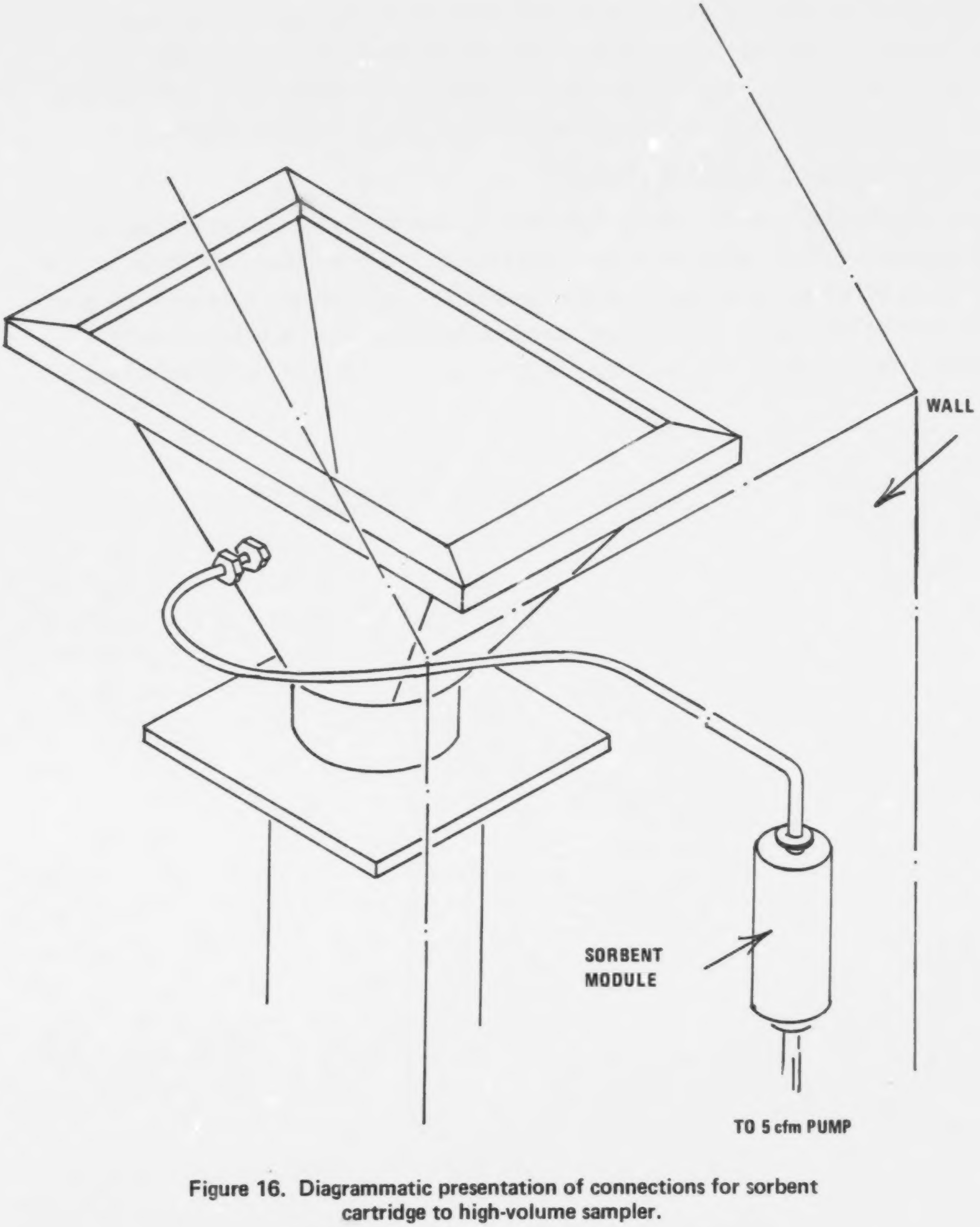

WALL
SORBENT MODULE
TO 5 cfm PUMP

Figure 16. Diagrammatic presentation of connections for sorbent cartridge to high-volume sampler.

may often be obtained at a single site location using any of a variety of commercially available vane type direction transmitters, cup anemometer speed transmitters, and thermocouple or thermistor temperature transmitters to provide continuous records on appropriate strip chart recorders.

5.3.2 Waterborne Fugitive Emissions

Stormwater runoff flowing overland is sampled using polyethylene, or preferably Teflon, plug collectors similar to the one shown in Figure 17. A network of plugs is driven into the ground so that the top face of each plug is just below the surface of the surrounding material. Overland runoff enters each plug through a screen in the top that removes large entrained

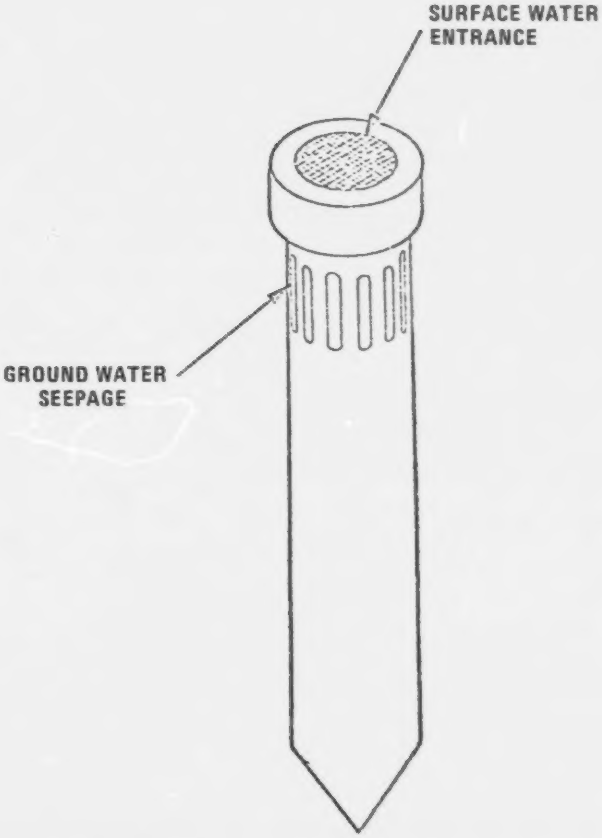


Figure 17. Stormwater runoff sampling plug collector.

particles but permits smaller suspended particulates to pass. These plugs may also be used to collect groundwater seepage through channels around the side surfaces by covering the openings in the top faces.

Stormwater runoff flowing in open channels can be sampled with plug collectors if the flow rate is low, with an automatic sampler, or by dipping collection bottles directly into the flowing stream. See Chapter 6 on liquids for more details. In all instances, the sample for organic compounds should be transferred to a dark glass bottle as soon after collection as possible.

Rainfall is measured during the sampling period by making visual observations of a standard rain gauge at frequent intervals or by using a recording gauge to provide a continuous record of rainfall rate. The resultant overland runoff flow is estimated by multiplying the area drained by the rainfall, either as total flow or a flow rate. An alternate method of estimating the overland runoff is to measure the increased flow in the open channels receiving it. Open channel runoff flow may be measured in a channel using appropriate portable weirs or flumes installed as close to the sampling points as possible.

5.4 SAMPLING PROGRAM PLANNING AND PERFORMANCE (refs. 1, 6, 36-44, 46-50)

A number of subjective evaluations may be required in determining which sources are to be included in the assessment program and how they can best be evaluated. The primary consideration for any source of fugitive emissions is whether the emissions will migrate beyond the site boundaries. If the planner is uncertain that the emissions from a specific source will have an impact upon the ambient air outside the site, it is probably best to exclude that source from individual source measurements and assume that its emissions will be accounted for in the site source sampling data. If such an assumption is made, the site source sampling methodology must be capable of detecting all expected source compound classes. In categorizing specific sources, those which are not clearly identifiable should be assigned to the more general open source class to insure that reasonable overall measurements are made rather than chance missing important data by sampling too specifically. Consideration must also be given to eliminating specific sampling of sources whose emission characteristics or physical arrangements are such that sampling can be conducted only under very limited conditions. In such cases, the source emissions can again be assumed to be included in the site source sampling data.

Sampler locations for enclosed or semienclosed sources will usually be limited to one or possibly two alternatives that will permit the use of the SASS train because the plume from such partially or fully enclosed sources will normally only reach the atmosphere via a prescribed path. The SASS train probe should be inserted into the plume as close to the source as possible to minimize the required sampling duration.

Upwind samplers for site sources should be located as close to the site boundary as possible to insure a reasonable estimate of background conditions. Downwind samplers should be located far enough away from specific sources at the site to eliminate any bias that might be introduced into the measurements. Ideal locations for downwind samplers that will insure sampling of a heterogeneous site source will usually be some distance downwind of the site boundary, but should be close enough to provide a useful sample size in a reasonable sampling period. The standard sampling duration is 8 hours of exposure time.

Stormwater runoff plugs should be installed as close to the source of pollution as possible, typically at the base of storage piles where overland flow is expected to be reasonably heavy and representative in makeup of the total source runoff. Open channel runoff dip sampling should be planned so as to avoid pool areas where suspended particulates may settle or highly turbulent areas where suspended particulates may be exaggerated. Other samplers such as the Quantum Science Limited automatic liquid sampler (U.S. distributor--Kahlsico, El Cajon, CA) may be used advantageously in these circumstances.

In preparing for the performance of the sampling program, the field staff will utilize the information provided in the program plan and pretest site survey to select the sampler locations best suited to the conditions during the sampling period.

Once the samplers are satisfactorily installed, the sampling program is carried out according to the schedule established in the program plan using the procedures for the collection and handling of samples described in this manual. The collected samples are analyzed onsite and/or delivered to the appropriate laboratory for analyses to determine their composition. The organic and inorganic methods specified in this manual are to be used.

5.5 DATA REDUCTION

The analytically determined compositions, concentrations, and densities of the sampled emissions are combined with the appropriate parameters of flow rate, temperature, and flow direction of their transporting air to yield quantitative concentrations at each sampling location. Measured background concentrations are then subtracted. The remaining concentrations are used in appropriate diffusion equations to calculate the contribution from each source of airborne materials. A library of computer programs is maintained at the User's Network for Applied Methods of Air Pollution (UNAMAP) at the Environmental Protection Agency's Research Triangle Computer Center to assist in the calculations.

Stormwater runoff pollutant concentrations are plotted against the measured flow rates or as a function of time against the measured rainfall rate to provide, by extrapolation, an estimate of the amount of any given material that can be expected to be conveyed to a receiving body for any given rainfall. Historical rainfall data can then be used to provide an estimate of seasonal or annual materials transfer.

CHAPTER 6

LIQUID AND SLURRY SAMPLING AND CHEMICAL ANALYSIS

6.1 INTRODUCTION (refs. 56-58)

In any given industrial process operation, the probability is high that a number of the influent and/or effluent streams will exist in liquid or slurry form. Considering the multiplicity of liquid streams in typical plants, the number of possible sampling points becomes extensive. The method chosen for Level 1 sampling is discussed below.

Once the samples are collected, they are analyzed onsite or packaged for shipment and analysis at the laboratory (see Chapters 8 and 9). Streams may be organic or aqueous or may contain water/organics/solids in miscible or immiscible fractions. The handling of these solutions will affect the reliability of the chemical or biological tests performed. Section 6.3 proposes a field separation scheme to prevent sample loss or adulteration. This scheme is comprehensive enough to prevent sample loss, but is simple enough to implement in the field.

6.2 PREPARING FOR SAMPLE COLLECTION

6.2.1 Personnel Requirements (ref. 59)

The liquid sampling techniques presented in this chapter are uncomplicated, and under favorable conditions only one person is needed to perform the sampling effort. There are situations, however, that will require additional manpower. Many streams will require that a crew member work under conditions or in areas where the potential for physical mishap is high. An additional crew member should be present to insure the safe completion of the task even though his active presence is not necessary for the sampling effort.

6.2.2 Dipper Sampling (refs. 31, 60-63)

The dipper sampling procedure is applicable to sampling sluices or open discharge streams. The dipper is made with a flared bowl and an attached handle long enough to reach the sluice or discharge areas. The bowl portion must be coated with Teflon. A dipper sample is obtained by inserting the dipper into the free-flowing stream so that a portion is collected from the full cross section of the stream.

The pretest site survey will produce information on process cycles so that the sampling times and points cover the most representative periods and locations of discharge. The total amount of sample collected for chemical analysis should be approximately 0.1 percent of the total stream flow up to a maximum of 20 L. All individually collected samples from a given site should be combined to produce one composite sample representing a complete time integration. Individual aliquots are drawn from the composite for further analysis. Whenever bioassay testing is programmed, greater volumes of sample are required, i.e., 200 L for toxicity to fathead minnow.

6.2.3 Automatic Sampling

There are several types of automatic sampling devices that may be employed in obtaining representative liquid samples for analysis. Some are flow-proportional and others provide time-averaged samples. Options are available for discrete increment collection and for refrigerated sample holding. Depth-integrated samples may also be gathered using other instruments. The type and advantage of these sample-gathering aids is site-dependent. Their use is encouraged whenever it might improve the data quality.

6.2.4 Heat Exchange Sampling Systems for High Temperature Lines

Many industrial systems utilize steam in their process applications. Uses ranging from relatively clean steam power plant operations to polluted lines resulting from stripping operations involving acid units, catalyst regeneration, and scrubbing of polluted gas streams will be encountered. In addition to pressurized process lines, various other process operations exist that contain superheated vapors composed of effluents generally characterizable as reaction products. The sampling techniques described in this section pertain to all of the above systems; however, for the sake of brevity, the term high temperature (HT) line will be used to represent all applications unless otherwise indicated.

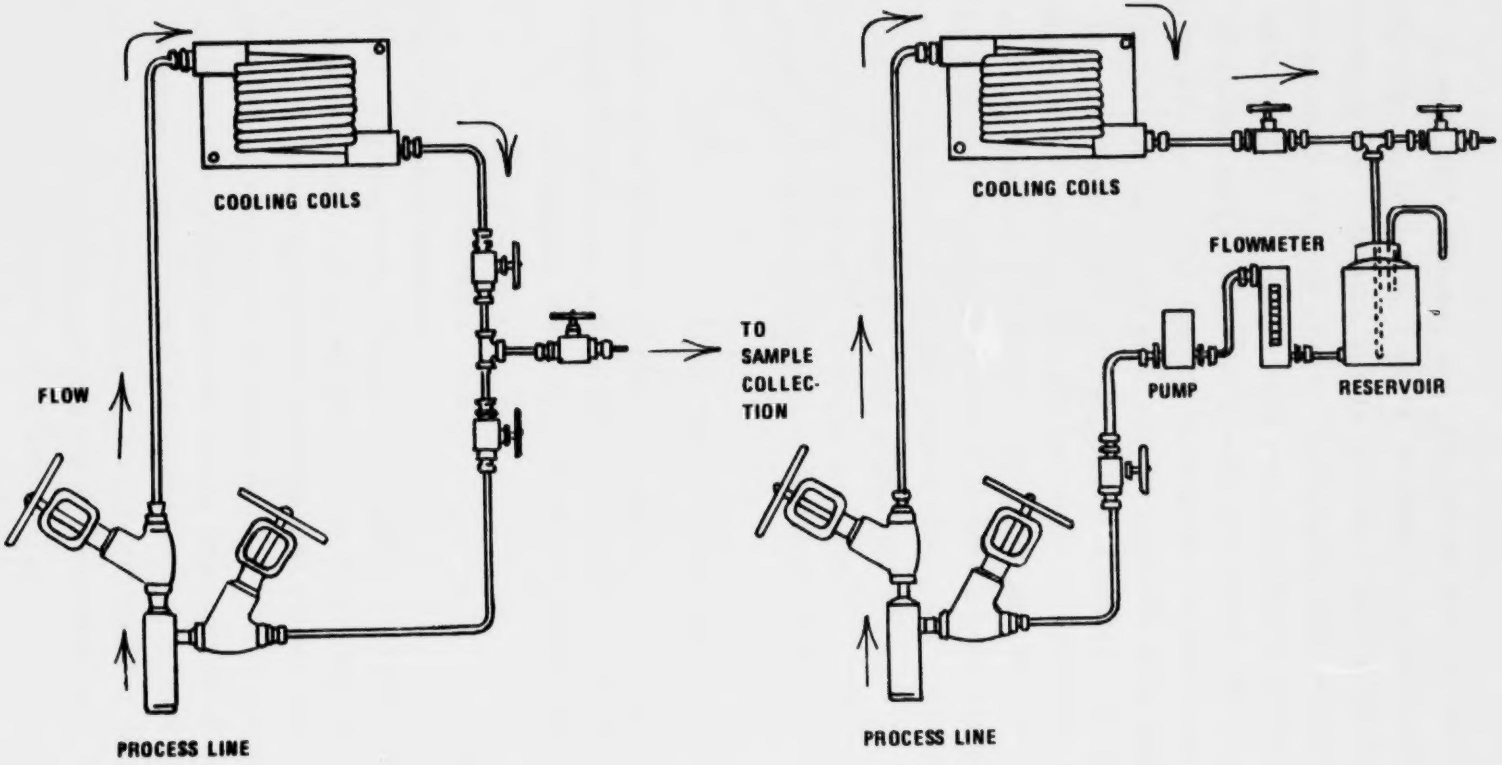
The principle used in the sampling of HT lines involves the use of a water-cooled condenser system. Typical examples of apparatus used for this purpose are illustrated in Figure 18. As can be seen in Figure 18, two approaches are possible depending on whether the pressure in the line is above or below atmospheric pressure. The condensate from the stream is collected in a reservoir for later analysis.

In sampling HT lines, it should be kept in mind that stream constituents will to some degree dissolve any substance contacted. For this reason, the area of the surfaces exposed to the sample and the time that the sample is in contact with these surfaces should be kept to a minimum. All tubing, valves, nozzles, and containers must be constructed from materials of sufficient strength to withstand the full pressure of the stream being sampled. Tubing diameter must be small enough so that storage within coils and tubing and the resultant time lag of the sample through the system are minimal. The sampling operations presented in this section may be used safely provided that proper caution is exercised.

6.2.5 Tap Sampling (ref. 52)

Contained liquids may be divided into two broad categories: those that are in motion (lines) and those that are not (tanks or drums). Usually, a specific sampling technique, such as stratification, is applied to each of these categories in order to accommodate the differences in sample characteristics. A flowing stream containing particulate matter may be stratified. A tank sample may also be stratified, but in the static sense rather than in the fluid sense. Moving streams are traditionally sampled using a technique called continuous sampling. This involves sample removal from a tap connected to a probe inserted into the line. Static liquid samples (tanks or large drums) are sampled using a technique called tap sampling.

For Level 1 purposes, the effort of inserting a probe into the line is too time-consuming to be efficient. Consequently, all contained liquids will be sampled using the tap method, as per ASTM D-270 (ref. 62), unless an in-line probe already exists. Tap sampling, as discussed in this chapter,


COOLING COILS
FLOW
PROCESS LINE
TO
SAMPLE
COLLEC-
TION
COOLING COILS
FLOWMETER
PUMP
RESERVOIR
PROCESS LINE

NATURAL CIRCULATION SAMPLING SYSTEM
(HIGH PRESSURE, HIGH TEMPERATURE)

FORCED INJECTION SAMPLING SYSTEM
(SUBATMOSPHERIC PRESSURE, HIGH TEMPERATURE)

Figure 18. Sampling apparatus for high pressure high temperature lines.

refers to a wide variety of grab techniques. In general, this type of sampling implies that a sample is taken at a tap from a line or tank wall. This approach is used for moving liquid or slurry streams. The procedure is also applicable to streams under pressure or having elevated temperature, provided the proper safety precautions are exercised. For systems under pressure, valves should be opened very slowly to avoid injury caused by sudden surge due to entrained air pockets or accumulated solids around the valve opening. Streams with elevated temperatures should be sampled using a heat exchanger system such as the one described in ASTM D-270 (ref. 62).

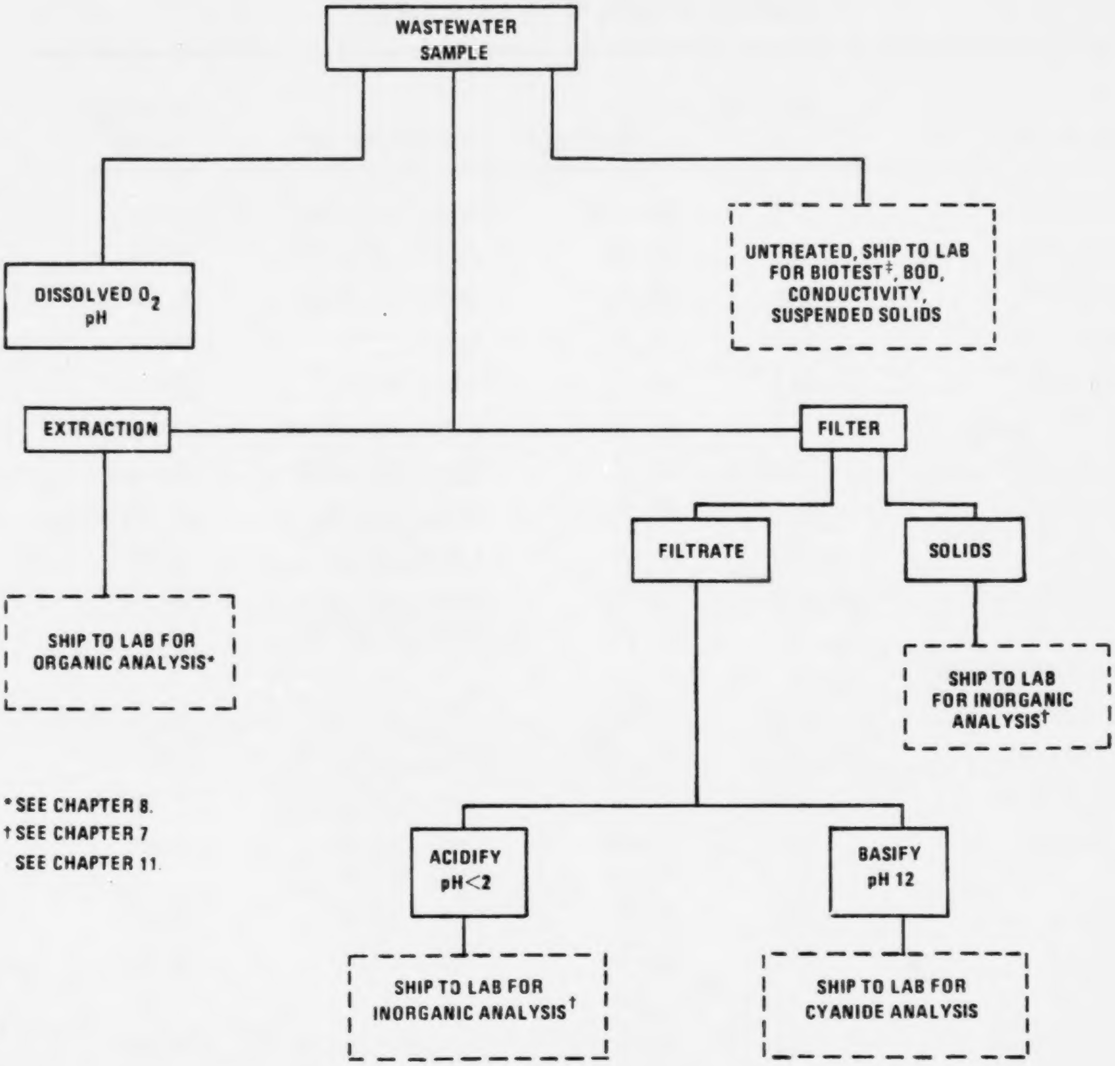
Tap samples are collected by inserting the sample line (a thoroughly washed Teflon line) into the sampling bottle so that it touches the bottom (after first flushing the sample line at a rate high enough to remove all sediment and gas pockets). The sample bottle should be thoroughly rinsed with sample prior to filling and the sample line flow must be regulated so as not to exceed 500 mL/min. If sampling valves or stopcocks are not available, samples may be taken from water-level or gauge-glass drain lines or petcocks.

6.3 LIQUID SAMPLE HANDLING AND SHIPMENT (ref. 64)

As mentioned previously in Section 6.1, sample handling is an important consideration where liquids are involved. The entire spectrum of liquid samples exists within the bounds of the following six categories:

a. Aqueous
b. Aqueous/organic
c. Organic
d. Aqueous/solid
e. Organic/solid
f. Aqueous/organic/solid

Figure 19 shows a field handling scheme for liquid/slurry samples. Certain of these samples must be stabilized prior to shipment for laboratory analysis; Table 12 presents the most recent EPA-approved procedures for this sample preservation. Consideration must also be given to the manner in which the samples are to be packed and conveyed to the testing laboratory since Department of Transportation regulations restrict shipment of certain materials on commercial carriers (see ref. 65 for details on the chemicals involved and packaging required). After preservation and packing, samples will be shipped


WASTEWATER SAMPLE
DISSOLVED O_2 pH
UNTREATED, SHIP TO LAB FOR BIOTEST[‡], BOD, CONDUCTIVITY, SUSPENDED SOLIDS
EXTRACTION
FILTER
FILTRATE
SOLIDS
SHIP TO LAB FOR ORGANIC ANALYSIS*
SHIP TO LAB FOR INORGANIC ANALYSIS[†]
ACIDIFY pH<2
BASIFY pH 12
SHIP TO LAB FOR INORGANIC ANALYSIS[†]
SHIP TO LAB FOR CYANIDE ANALYSIS

* SEE CHAPTER 8.
† SEE CHAPTER 7
SEE CHAPTER 11.

Figure 19. Sample handling summary.

TABLE 12. RECOMMENDATION FOR SAMPLING AND PRESERVATION OF SAMPLES ACCORDING TO MEASUREMENT[1]

Measurement	Volume required (mL)	Container[2]	Preservative	Holding time[3]
Acidity	100	P, G	None required	24 h
Alkalinity	100	P, G	Cool, 4° C	24 h
Arsenic	100	P, G	HNO_3 to pH <2	6 mo
BOD	1000	P, G	Cool, 4° C	24 h
Bromide	100	P, G	Cool, 4° C	24 h
COD	50	P, G	H_2SO_4 to pH <2	7 days[4]
Chloride	50	P, G	None required	7 days
Chlorine	200	P, G	Det. onsite	No holding
Color	50	P, G	Cool, 4° C	24 h
Cyanides	500	P, G	Cool, 4° C NaOH to pH 12	24 h
Dissolved oxygen				
Probe	300	G only	Det. onsite	No holding
Winkler	300	G only	Fix onsite	4-8 h
Fluoride	300	P, G	None required	7 days[5]
Hardness	100	P, G	Cool, 4° C HNO_3 to pH <2	6 mo
Iodide	100	P, G	Cool, 4° C	24 h
MBAS	250	P, G	Cool, 4° C	24 h
Metals				
Dissolved	200	P, G	Filter onsite HNO_3 to pH <2	6 mo[6]
Suspended			Filter onsite	6 mo
Total	100		HNO_3 to pH <2	6 mo[6]
Mercury				
Dissolved	100	P, G	Filter	38 days (glass) 13 days (hard plastic)

See footnotes at end of table. (continued)

TABLE 12 (continued)

Measurement	Volume required (mL)	Container[2]	Preservative	Holding time[3]
Total	100	P, G	HNO_3 to pH <2	38 days (glass) 13 days (hard plastic)
Nitrogen				
Ammonia	400	P, G	Cool, 4° C H_2SO_4 to pH <2	24 h[4]
Kjeldahl, total	500	P, G	Cool, 4° C H_2SO_4 to pH <2	24 h[4] [7]
Nitrate	100	P, G	Cool, 4° C H_2SO_4 to pH <2	24 h
Nitrite	50	P, G	Cool, 4° C	48 h
NTA	50	P, G	Cool, 4° C	24 h
Oil & grease	1000	G only	Cool, 4° C H_2SO_4 or HCl to pH <2	24 h
Organic carbon	25	P, G	Cool, 4° C H_2SO_4 to pH <2	24 h
pH	25	P, G	Det. on site	6 h
Phenolics	500	G only	Cool, 4° C H_3PO_4 to pH <4 1.0 g $CuSO_4$/L	24 h
Phosphorus				
Orthophosphate, dissolved	50	P, G	Filter onsite Cool, 4° C	24 h
Hydrolyzable	50	P, G	Cool, 4° C H_2SO_4 to pH <2	24 h[4]
Total	50	P, G	Cool, 4° C H_2SO_4 to pH <2	24 h[4]
Total, dissolved	50	P, G	Filter onsite Cool, 4° C	24 h[4]

(continued)

TABLE 12 (continued)

Measurement	Volume required (mL)	Container[2]	Preservative	Holding time[3]
Residue				
Filterable	100	P, G	Cool, 4° C	7 days
Nonfilterable	100	P, G	Cool, 4° C	7 days
Total	100	P, G	Cool, 4° C	7 days
Volatile	100	P, G	Cool, 4° C	7 days
Settleable matter	1000	P, G	None required	24 h
Selenium	50	P, G	HNO_3 to pH <2	6 mo
Silica	50	P only	Cool, 4° C	7 days
Specific conductance	100	P, G	Cool, 4° C	24 h[8]
Sulfate	50	P, G	Cool, 4° C	7 h
Sulfide	500	P, G	2 mL zinc acetate	24 h
Sulfite	50	P, G	Det. onsite	No holding
Temperature	1000	P, G	Det. onsite	No holding
Threshold odor	200	G only	Cool, 4° C	24 h
Turbidity	100	P, G	Cool, 4° C	7 days[9]

See footnotes on following page.

[1] Source of this table is the National Environmental Research Center, Cincinnati, Ohio (ref. 66). More specific instructions for preservation and sampling are found with each procedure as detailed in this manual. A general discussion on sampling water and industrial wastewater may be found in ASTM, Part 31, pp. 72-82 (1976) Method D-3370.

[2] Plastic (P) or glass (G). For metals, polyethylene with a polypropylene cap (no liner) is preferred.

[3] It should be pointed out that holding times listed above are recommended for properly preserved samples based on currently available data. It is recognized that for some sample types extension of these times may be possible, while for other types these times may be too long. Where shipping regulations prevent the use of the proper preservation technique or the holding time is exceeded, such as in the case of a 24-h composite, the final reported data for these samples should indicate the specific variance.

[4] Data obtained from National Enforcement Investigations Center, Denver, Colorado, support a 4-week holding time for this parameter in Sewerage Systems (SIC 4952).

[5] SDWA permits holding time of 1 month.

[6] Where HNO_3 cannot be used because of shipping restrictions, the sample may be initially preserved by icing and immediately shipped to the laboratory. Upon receipt in the laboratory, the sample must be acidified to a pH 2 with HNO_3 (normally 3 mL 1:1 HNO_3/L is sufficient). At the time of analysis, the sample container should be thoroughly rinsed with 1:1 HNO_3 and the washings added to the sample (volume correction may be required).

[7] SDWA permits holding time of 14 days.

[8] If the sample is stabilized by cooling, it should be warmed to 25° C for reading, or temperature correction made and results reported at 25° C.

[9] SDWA requires analysis within 1 hr.

by the most expeditious manner possible, and will not be delayed unnecessarily. Whenever there is danger of exceeding the recommended holding times, consideration should be given to enlisting the services of a qualified commercial testing facility nearer the sampling site to perform the time-sensitive analyses.

Aqueous samples for organic content determination are first extracted in convenient aliquots with high purity liquid chromatography grade methylene chloride equal to 10 percent by volume of the aliquot to be extracted. Each aliquot should be extracted two times at acid and alkaline pH (see Section 9.3.1). Following extraction, the individual volumes of methylene chloride from the total sample are recombined to form one organic fraction for further analysis. The above extraction may be performed in the laboratory or the field, whichever is more convenient and most advantageous from the analytical standpoint.

Filtration of the sample for suspended solid determination should be performed using a preweighed Reeve Angel 934-A or 984 H or Gelman type A glass fiber filter. This filtration procedure may be performed more efficiently in the laboratory when the suspended solids content is high enough to block the filter. When such is the case, provision must be made to transport the cooled sample to the lab within the time frame of the most sensitive test parameter to be determined. The filtrate from this process may be used for anion and elemental analysis.

6.4 LIQUID ANALYSIS (ref. 67)

Certain liquid parameter analyses must be performed onsite for results to accurately reflect the existing conditions. Such measurements as temperature, pH, chlorine, ammonia, sulfide, dissolved oxygen, and other readily changing concentrations may be determined in situ using calibrated thermocouples, standardized selective ion electrodes, and other sensors. When there are no positive or negative matrix interferences, acceptable data (for Level 1 purposes) may be produced using commercially available test kit methods and freshly collected sample. Other liquid parameters such as sulfate, phosphate, nitrate, nitrite, carbonate, chloride, fluoride, cyanide, etc., may be determined in the field by test kit methods or preferably at the laboratory using ion chromatography procedures and appropriately preserved samples. (See Table 12.) In either instance, perform these analyses according to the equipment manufacturer's specifications and in conjunction with known standard concentrations as a quality control measure.

Biochemical oxygen demand, chemical oxygen demand, suspended solids, alkalinity, and acidity testing should be performed on unfiltered sample aliquots using recognized techniques. Conductivity measurements may be performed on either a filtered or unfiltered aliquot.

CHAPTER 7

SOLID SAMPLING

7.1 INTRODUCTION (refs. 10, 67-69)

Solid sampling covers a broad spectrum of material sizes from large lumps to fine powders and dusts. There is an equally diverse assortment of potential sample sites including railroad cars, barges, trucks, large heaps, plant hoppers, and conveyor belts. Obviously, no one sampling method or piece of equipment can accommodate all possible situations. Furthermore, all of the above sampling locations may contain products of widely varying consistency. For the purposes of this chapter, the consistency of solid samples ranges, by definition, from anhydrous or dry solids to thick, nonflowing pastes.

The recommended Level 1 sampling technique is the modified grab sample. This sample shall be taken with care to insure its representative nature and may be composed of a time- or space-integrated series of smaller samples to achieve this end. In general, the Level 1 and Level 2 solid sampling techniques are identical except that, in the case of Level 2 sampling, a series of grab samples is taken over a longer period of time from a conveyor belt or over a larger area for stationary storage sites such as railroad cars or large heaps. In cases of extreme sample variability, a larger grab sample consisting of several increments or shovelfuls is required in Level 1. In most cases, the difference between the Level 1 sample and a time-averaged Level 2 sample is only a matter of degree rather than of technique.

The following sections present the sampling approaches applicable to input and output solid streams and storage piles.

7.2 SOLIDS SAMPLING PROCEDURES

Level 1 solid sampling procedures use three manual grab sampling techniques: shovel or grab sampling; boring techniques, which include pipe or thief sampling; and auger sampling. Data obtained from the pretest site survey concerning the physical characteristics of the sample, together with the optimum choice of sampling location, will determine the appropriate sampling technique. Table 13 presents a sampling scheme showing the appropriate sampling technique as a function of physical characteristics and actual location of the sampling points.

Each of the grab sampling techniques is discussed in detail in the sections to follow.

7.2.1 Shovel Grab Sampling (refs. 33, 68, 70-74)

Raw material piles of relatively coarse lump size (ore piles, aggregate piles, coal feed, etc.) are sampled using a fractional shoveling technique. The shovel used in this procedure is of the square-edged variety measuring 12 in. wide.

In sampling from belt conveyors, one full cross section the width of the shovel blade is taken as the sample.

Where ladder or tray conveyors are sampled, one shovelful from one compartment is removed.

Screw conveyors transfer sludge-type materials (such as ash effluents) and are usually enclosed systems. The optimum sampling point for these systems is the conveyor exit. If this point is located in an unreachable position, the sample must then be withdrawn from the entrance or exit area, depending on whether the stream is influent or effluent, using a pipe, thief, or auger technique (Section 7.2.2).

Duct conveyors consist of either gravity feed systems or chain-driven scrapers and may be open-top or enclosed depending on the fineness of the solid being transported. Open duct conveyors are sampled by removing one shovelful of material from the top via the adjoining catwalk. Closed ducts are sampled by taking one shovelful from the exit point. If these points are unreachable, the sample must be taken from the storage pile using a pipe, thief, or auger (Section 7.2.2).

7.2.2 Boring Techniques (refs. 33, 67, 75)

Pipe borers represent another class of solid sampling methods applicable to materials stored in piles, silos, or bins. The pipe is inserted

TABLE 13. LEVEL 1 METHODS FOR SOLID SAMPLING

Physical nature of sample	Belt conveyors	Ladder tray conveyor	Screw conveyor	Duct sample	Open piles	Storage bins or silos
Fine powder	N/A	Shovel grab from one tray	One shovel from point of exit	One shovel from exit if enclosed, from top if open	Pipe or thief	Pipe or thief
Coarse powder	N/A	Shovel grab from one tray	One shovel from point of exit	Pipe, from exit if enclosed, from top if open	Pipe, thief, or auger	Pipe, thief, or auger
Coarse grain	Cross stream cut, one shovel	Shovel grab from one tray	N/A	One shovel from exit if enclosed, from top if open	Auger	Auger
Lump	Cross stream cut, one shovel	N/A	N/A	N/A	Four shovels, one from each side	Shovel or auger

into the material to be sampled at regular intervals. The method is fairly reliable, providing that the pipe is long enough to reach the bottom of the material. However, it is only applicable to fine or powdered dry materials, because lumps or any stickiness will jam or plug the pipe. Small pipe borers can be used to sample material in sacks or cans. There are primarily two pipe designs that give best results. One is a simple pipe that is tapered so the end first inserted is smaller in diameter than the handle end. A more sophisticated design, known as a thief, makes the sample more representative vertically. It consists of two close-fitting concentric pipes sealed at the base in a conical point. Longitudinal slots are cut along the side of each pipe. The thief is inserted with the slots turned away from each other and then, when the sampler is in position, the outer pipe is rotated, lining up the slots and allowing the inner pipe to fill with sample. For proper results with any design of pipe borer, the opening through which the sample material passes (slots or circular pipe ends) must be larger than the largest particle size.

Auger samplers, a form of drill, pack the sample in the helical groove of the auger and can be enclosed in a casing if the nature of the sample is such that it will spill when the auger is removed from the hole. Like pipe borers, they are simple to use and have the further advantage of being applicable to a greater variety of materials. For example, augers work well for materials that are packed too hard for the insertion of a pipe sampler. For tightly packed materials, machine-driven augers are available. However, if spillage is a serious problem, a thief type pipe sampler is the better choice.

7.3 SAMPLE COLLECTION AND STORAGE (refs. 7, 33, 70, 72-76)

It is always preferable to sample a moving stream either in pipes or off conveyor belts rather than from stationary storage sites. This is particularly true if the sample has a wide particle size distribution. Stored containers or heaped beds of material tend to settle, segregating the particles according to size and density, and it is difficult to compensate for this bias during sampling. Furthermore, large masses of stored material are extremely difficult to handle. The interior portions are relatively inaccessible, and the amount of time and space needed to move the material enough to take a representative sample can become prohibitive. However, such situations can generally be avoided by a good sampling plan.

Typically, in a test for trace elements, the solid materials of interest associated with a process are the feed materials and the residues from particulate matter scrubbers such as baghouses, high energy venturis, and electrostatic precipitators. Raw feed stock, as it passes through the process stream, may pick up other materials as contaminants and therefore differs greatly in composition from the final feed to the process. Consequently, samples should be taken at the last possible site before the stream is fed into the process. This means that sampling will generally be conducted from a feed hopper, if accessible, or from the pipes or conveyors that feed the materials to the process. Similarly, scrubber residues can be sampled from the collection hopper or from pipes going to the hopper. Extra handling steps only increase the chances of the sample becoming contaminated.

When samples are taken from conveyor belts, the standard procedure is to stop the conveyor at regular intervals (e.g., every 10 or 15 min) and shovel off a section of the material. Flat-nosed shovels with straight perpendicular sides are best for this type of sampling.

Samples collected in accordance with the above-prescribed procedures should be stored in air-tight, glass containers with Teflon lids until ready for analysis. If larger samples are necessary to provide a representative sample, they should be placed in a series of these containers.

CHAPTER 8

LEVEL 1 INORGANIC LABORATORY ANALYSIS TECHNIQUES

8.1 INTRODUCTION

The inorganic species to be measured in the Level 1 program include certain inorganic gases; the major, minor, and trace element constituents of a variety of samples; and certain simple and complex anions. Some of these species will be measured in the field; the majority, however, will be measured in the laboratory.

The samples to be analyzed include gases, liquids, and solids (see Figures 1 and 2). Inorganic gases to be measured are SO_2, SO_3, NO_x, CO, CO_2, O_2, N_2, H_2S, COS, NH_3, HCN, and $(CN)_2$. These gases are to be measured in the field using gas chromatographic, spectrophotometric, and wet chemistry procedures. The details of these procedures are provided in Chapter 3. Both organic and aqueous liquids will be collected and analyzed. Solids to be analyzed will include bulk solids and those filtered from liquid media. An important source of liquid and solid samples will be the SASS and FAST trains (see Chapters 4 and 5).

Elemental analyses are to be carried out in the laboratory on both liquid and solid samples. Spark source mass spectrometry (SSMS), ion chromatography (IC), and atomic absorption spectrometry (AAS) are to be used in this work. SSMS will be used for the analysis of the vast majority of the elements. AAS will be used for all Hg determinations and for Sb and As quantitation of the second and third SASS impinger solutions. IC is to be used for the determination of the species F^-, Cl^-, NO_2^-, NO_3^-, $SO_3^=$, $SO_4^=$, and $PO_4^{\equiv}$. The type of commercial test kit discussed in Chapter 6 may be used rather than IC for determination of these ions if permitted by the EPA project officer.

8.2 SAMPLE PREPARATION AND ANALYSIS

The following text describes the protocols to be used in the analysis of a variety of samples. These protocols are schematically represented in Figures 20 and 21. It is assumed here that sample allocation has taken place, that is, that the samples collected in the field have been apportioned for the various analyses including organic analyses, inorganic analyses, microscopy, and biotesting. Refer to Chapters 2 through 7 and especially Chapter 4 for instructions regarding allocation.

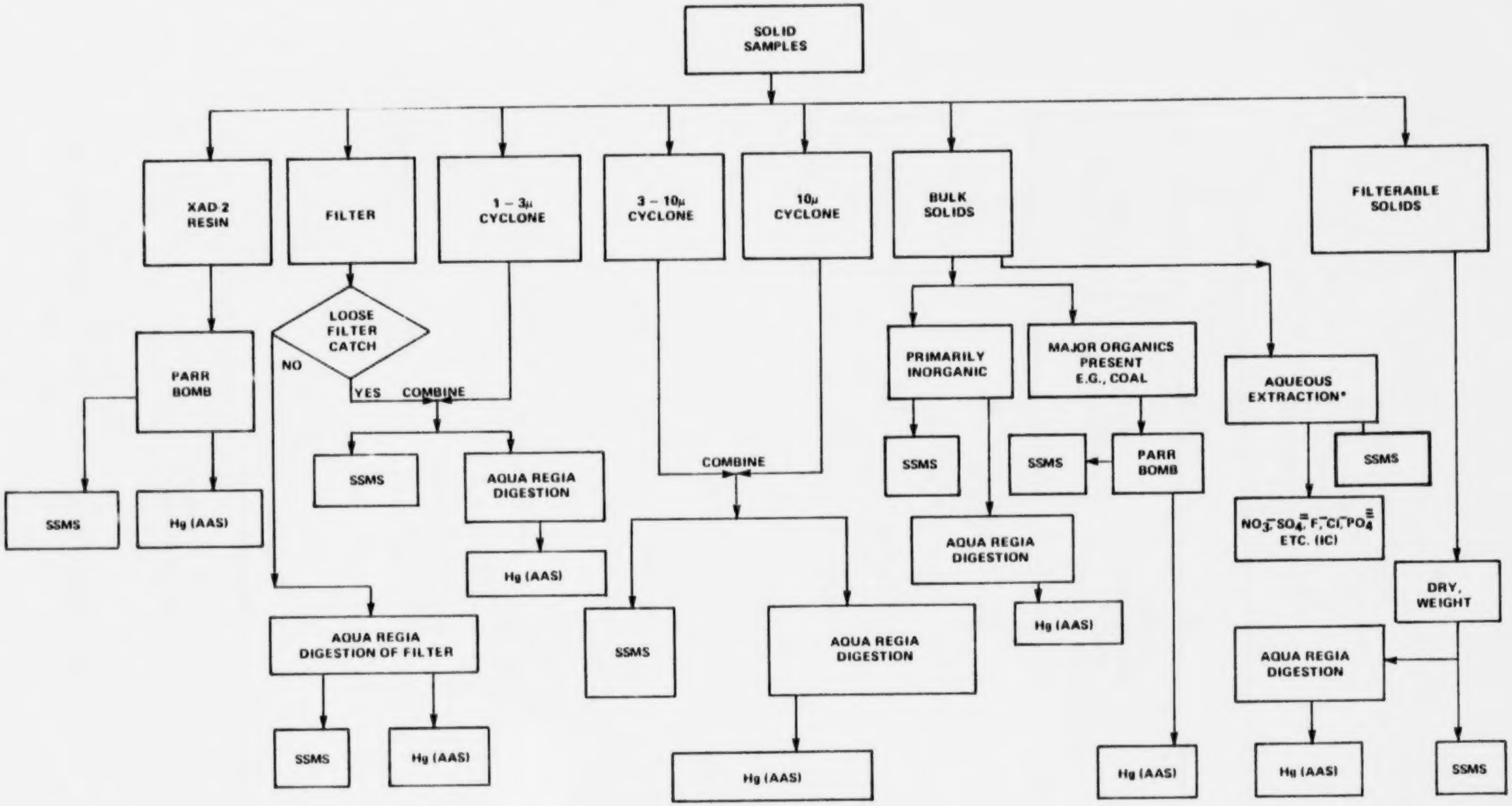
8.2.1 Gases

The inorganic gases listed above will be measured in the field using neat samples. Gases collected in traps in the SASS train are considered a part of the appropriate solid or liquid SASS train samples and are, accordingly, prepared as part of these latter samples.

8.2.2 Bulk Liquids

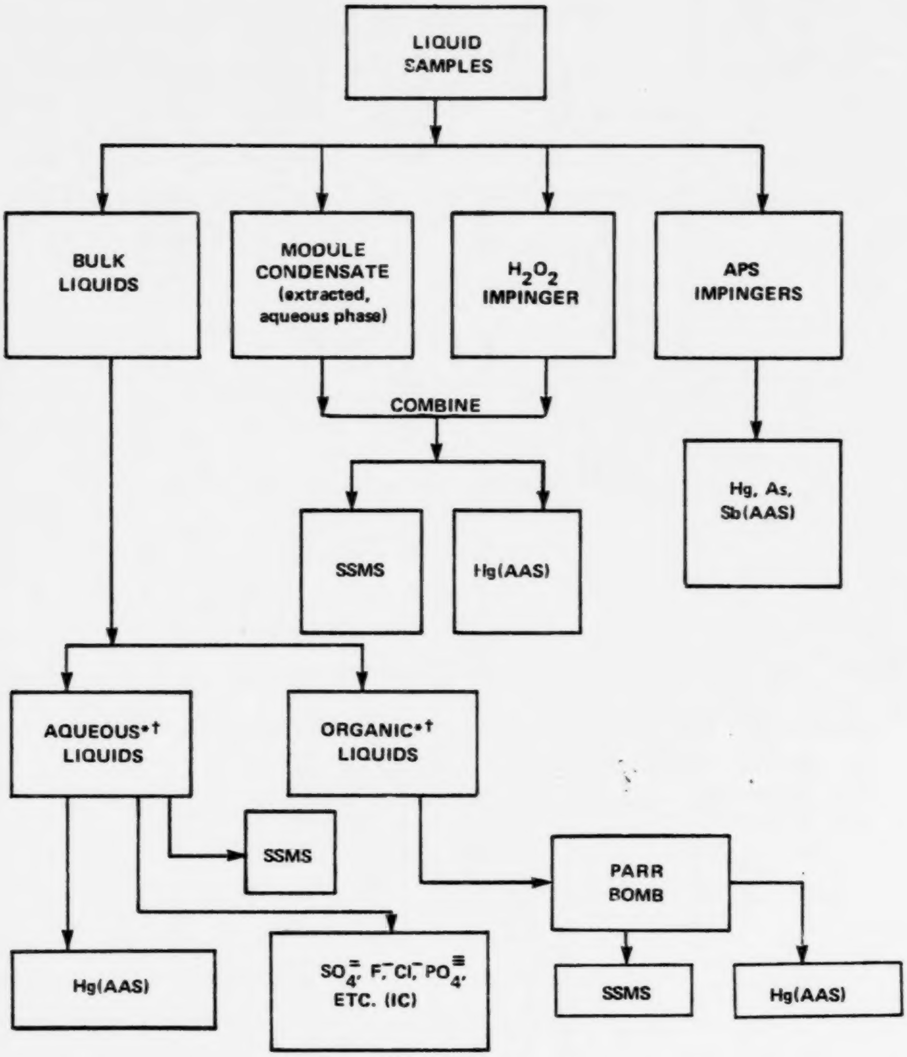
Two types of bulk liquids will be analyzed: organic and aqueous. Organic liquids will include fuels, feedstocks, and waste solvents. One gram of these liquids or a quantity having a heat of combustion <8.0 K calories, whichever is less, must be combusted or "ashed" prior to analysis for inorganic species. Use the Parr bomb procedure as outlined in Appendix C. The combusted sample is then analyzed for trace element content using SSMS and AAS as described above.

Aqueous bulk liquid samples should not usually require any preparation. The exception might be a water stream contaminated with high levels of organic residues. In this situation, the aqueous sample will have to be extracted with methylene chloride as described in Chapter 6. The organic extract will then have to be Parr bombed. Still another possibility is that the aqueous sample contains insoluble particulate material. This will have to be removed using filtration, also described in Chapter 6. The solids collected will need to be Parr bombed if they contain significant amounts of organic material (see Figure 20). The aqueous bulk liquid samples are to be analyzed for trace element and anion content using SSMS, AAS, and IC.


SOLID SAMPLES
XAD-2 RESIN
FILTER
1 – 3μ CYCLONE
3 – 10μ CYCLONE
10μ CYCLONE
BULK SOLIDS
FILTERABLE SOLIDS
PARR BOMB
LOOSE FILTER CATCH
NO
YES
COMBINE
PRIMARILY INORGANIC
MAJOR ORGANICS PRESENT E.G., COAL
AQUEOUS EXTRACTION*
SSMS
Hg (AAS)
SSMS
AQUA REGIA DIGESTION
COMBINE
SSMS
PARR BOMB
SSMS
NO3‾, SO4=, F‾, Cl‾, PO4≡ ETC. (IC)
Hg (AAS)
AQUA REGIA DIGESTION
DRY, WEIGHT
AQUA REGIA DIGESTION OF FILTER
SSMS
AQUA REGIA DIGESTION
Hg (AAS)
AQUA REGIA DIGESTION
SSMS
Hg (AAS)
Hg (AAS)
Hg (AAS)
Hg (AAS)
SSMS

*See Appendix E

Figure 20. Level 1 inorganic laboratory analysis plan for solid samples.


LIQUID SAMPLES
BULK LIQUIDS
MODULE CONDENSATE (extracted, aqueous phase)
H_2O_2 IMPINGER
APS IMPINGERS
COMBINE
SSMS
Hg(AAS)
Hg, As, Sb(AAS)
AQUEOUS*† LIQUIDS
ORGANIC*† LIQUIDS
SSMS
PARR BOMB
Hg(AAS)
$SO_4^=$, F^-, Cl^-, $PO_4^{\equiv}$, ETC. (IC)
SSMS
Hg(AAS)

*Liquids that are a mixture of water and organic substances must be separated using extraction.

†Solids present in either of these types of liquids will have to be removed by filtration and Parr bombed if they are, in part, organic.

Figure 21. Level 1 organic laboratory analysis plan for liquid samples.

8.2.3 Bulk Solids

Certain solids need no special preparation for analysis by SSMS. These include flyash, bottom ash, and inorganic minerals. Those solids that are principally organic must be combusted (using the Parr bomb technique) prior to SSMS analysis. For example, bulk organic materials and the XAD resin from the SASS train must be combusted to avoid interference in mass spectral analysis. Still other solids (e.g., coal) must be combusted, not so much to remove interferences but to concentrate the inorganic constituents. A more difficult question arises with "partially" organic samples. In these cases, the sample is to be analyzed by SSMS without combustion. If the resultant mass spectral data are not suitable for elemental analysis (i.e., element signals are masked), then the sample is to be combusted and reanalyzed by SSMS.

For the analysis of Hg (by AAS), the samples must be in solution form. The samples resulting from Parr bomb combustion are in such form, and thus are suitable for such analyses. Those samples that are not combusted must, accordingly, be treated so as to release Hg. Aqua regia digestions are used to dissolve these samples for Hg analysis. Also, particulate catches on the glass fiber filters taken from the SASS and FAST trains will generally be embedded in the pores of the filter and will require aqua regia digestion for the SSMS analysis as well as for the Hg analysis. The aqua regia digestion involves heating a mixture of the sample and aqua regia for about 6 h and refluxing the acid. (See Appendix D for further details.)

Leachable anions and cations are to be released from bulk solids using a cold water extraction procedure. The anions are to be determined using IC and the cations are to be determined using SSMS. The water extraction procedure is described in Appendix E. The anions to be determined include F^-, Cl^-, NO_2^-, NO_3^-, $SO_3^=$, $SO_4^=$, and $PO_4^{\equiv}$.

8.2.4 SASS Train Samples

Summaries of the SASS train sample analysis protocols are provided in Figure 10. Discussions of the procedures to be used with these samples follow.

8.2.4.1 Cyclone and Filter Catches--

The catches from the 10- and 3-μm cyclones are to be weighed separately and then combined. A portion of the resultant combination is taken for elemental analysis using SSMS. If the sample is high in organic content, it will have to be Parr bombed prior to SSMS analysis. Another portion of the combination (see Table 11) is to be digested in aqua regia. The resultant solution is analyzed for Hg using AAS.

Both the filter and the 1-μm cyclone catches are to be weighed. The second step in the analysis depends upon the nature of the filter catch, as described in Chapter 4. If the filter catch is loose, it is to be gently shaken or tapped from the filter and combined with the catch from the 1-μm cyclone. Appropriate portions of this combination are to be analyzed using SSMS and AAS as described in the preceding paragraph. If the filter catch cannot be released from the filter, the filter is first to be apportioned by cutting it into appropriate sections (see Chapter 4). The section for inorganic analysis is then digested in aqua regia and the resultant solution is analyzed using SSMS and AAS. When the filter is analyzed by itself, the 1-μm cyclone catch is also analyzed by itself using the same protocol as is used for the catch combinations described above.

8.2.4.2 Probe and Cyclone Washings--

The probe and cyclone washings combination is taken to dryness and weighed. If the dried sample exceeds 10 percent of the total cyclone and filter sample weight, then it is analyzed. Otherwise it is simply held in reserve. If the sample is to be analyzed, a portion of it is analyzed by SSMS. Again, a high organic content may require Parr bomb combustion prior to SSMS analysis. Another portion of the sample is digested in aqua regia and the resultant solution is analyzed for Hg using AAS.

8.2.4.3 XAD-2 Resin--

A 1-g portion of the homogeneously mixed XAD-2 resin is Parr bombed. The resultant solution is analyzed using SSMS and AAS*.

8.2.4.4 XAD-2 Resin Module Condensate--

The contents of the XAD-2 resin module condensate reservoir are extracted as described in Chapter 4. This extracted aqueous solution is then combined with the solution from the first impinger. The resultant combination is analyzed using SSMS and AAS*.

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* Only Hg by AAS.

8.2.4.5 APS Impinger Solutions--

The APS impinger solutions are combined and analyzed for Hg, Sb, and As using AAS.

8.3 ANALYTICAL METHODOLOGIES

8.3.1 Elemental Analysis by Spark Source Mass Spectrometry (refs. 77-87)

Spark source mass spectrometry (SSMS) has been chosen for elemental analysis because (a) it provides multielemental analysis wherein sensitivity does not vary greatly from element to element, and (b) the limit of detection is generally at the ppm level.

8.3.1.1 Instrumentation--

One source of difficulty in SSMS is the presence of organic materials in the sample. Such materials may lead to masking of the elemental ion signals by organic fragment ions. This problem is especially severe with samples that are principally organic in nature; such samples must be combusted as described above. However, certain samples that are in part organic will need combustion only if ion masking is significant. In order to minimize this ion interference, and thus the need for combustion, the instrumental resolution* is to be at least 3000 in the Pb^+ ion region; this value is chosen on the basis of experience in the Level 1 program.

Another instrumental concern is ion detection. There are two general types of SSMS detection systems: photographic plate and electrical detection. For Level 1 survey purposes, the photographic system will be applied. All photoplates acquired as a part of Level 1 studies are to be retained for a period of 2 years.

8.3.1.2 Electrode Preparation--

If the sample to be analyzed by SSMS is not already a conductor, it must be placed in a conducting medium (graphite). The graphite to be used shall be Ultra-1-N-USP from Ultracarbon Corporation, Bay City, Michigan, or a graphite of equal purity. Figure 22 shows in schematic form how each sample type is prepared for analysis by SSMS. Aqueous samples are prepared

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*Instrumental resolution is defined as $\bar{M}/\Delta M$, where $\bar{M}$ is the average mass of two ions just resolved (i.e., 50 percent valley between peaks) and ΔM is the difference in their masses.

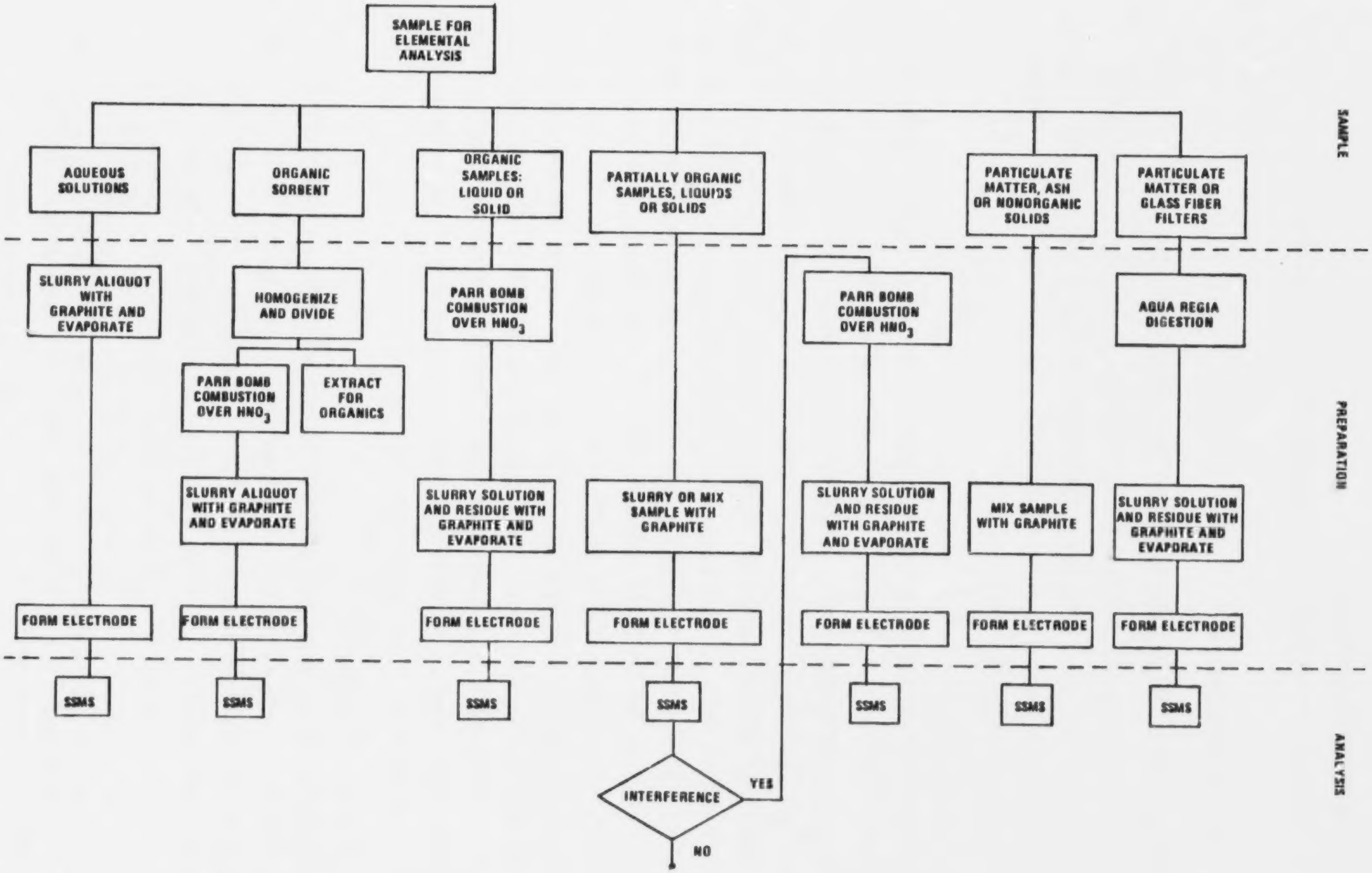

SAMPLE
PREPARATION
ANALYSIS
SAMPLE FOR ELEMENTAL ANALYSIS
AQUEOUS SOLUTIONS
ORGANIC SORBENT
ORGANIC SAMPLES: LIQUID OR SOLID
PARTIALLY ORGANIC SAMPLES, LIQUIDS OR SOLIDS
PARTICULATE MATTER, ASH OR NONORGANIC SOLIDS
PARTICULATE MATTER OR GLASS FIBER FILTERS
SLURRY ALIQUOT WITH GRAPHITE AND EVAPORATE
HOMOGENIZE AND DIVIDE
PARR BOMB COMBUSTION OVER HNO_3
EXTRACT FOR ORGANICS
SLURRY ALIQUOT WITH GRAPHITE AND EVAPORATE
PARR BOMB COMBUSTION OVER HNO_3
SLURRY SOLUTION AND RESIDUE WITH GRAPHITE AND EVAPORATE
SLURRY OR MIX SAMPLE WITH GRAPHITE
PARR BOMB COMBUSTION OVER HNO_3
SLURRY SOLUTION AND RESIDUE WITH GRAPHITE AND EVAPORATE
MIX SAMPLE WITH GRAPHITE
AQUA REGIA DIGESTION
SLURRY SOLUTION AND RESIDUE WITH GRAPHITE AND EVAPORATE
FORM ELECTRODE
SSMS
INTERFERENCE
YES
NO

Figure 22. Sample preparation for SSMS elemental analysis.

by mixing 50 mg of graphite and an internal standard with 1 to 20 mL of the sample. The amount of liquid used should be such that it yields 50 mg of dry residue. Alcohol may be added to promote carbon "wetting." The slurry formed is taken to dryness under a heat lamp. The remaining solid is mixed thoroughly and formed into a set of three electrodes (two for sparking plus a spare). Combusted, acid-digested, and water-extracted samples will be prepared for SSMS analysis in a manner analogous to that of the aqueous samples. Nonconducting solids not requiring combustion will simply be mixed in a 1:1 weight ratio with graphite. Again 50 mg of carbon, an internal standard, and 50 mg of sample are mixed and formed into an electrode set. If less than 50 mg of sample, either as a residue from a liquid sample or as a solid, is available, all the sample that is available should be used for electrode preparation.

8.3.1.3 Standards--

The method of internal standards is to be used for quantification in SSMS. Elements that shall be used as internal standards are erbium, indium, or rhenium. The standardization procedure involves first mixing one of these elements with a known multielement mixture. This multielement mixture should be prepared with commercially available oxides that are 99.99 or 99.999 percent pure. Commercially available mixtures (e.g., Spex Mix, Spex Mix, Inc., Metuchen, N.J.), are to be used for those elements for which pure oxides are unavailable.

Replicate standards of mid-range concentration are then prepared by diluting portions of this multielement mixture with graphite. (Single point standards are acceptable within the Level 1 framework.) These standards are then analyzed using the "just disappearing line" technique. This technique involves several steps. First, as the electrodes prepared from these samples are sparked, a series of photoplate exposures of variable, total charge accumulation are made. The plate is then developed and the charge values corresponding to the lines from the internal standard and the elements of interest just disappearing are noted. These charge values are then used to determine the relative sensitivity coefficients (S_R) of the elements of interest to the internal standard. (See Section 8.3.1.5 for sample calculation.)

8.3.1.4 Analysis of Environmental Samples--

As in the case of the standards, a known amount of an internal standard is added to the sample prior to electrode preparation. The unknown or test sample concentrations are determined by the "just disappearing line" technique, which in this case makes use of the S_R values determined previously with the standards. (See Section 8.3.1.5 for sample calculation.)

A matter of concern in using the "just disappearing line" technique is the nature of the variation in the total charge accumulation from exposure to exposure in the series. The maximum exposure for Level 1 work shall correspond to 300 nanocoulombs of charge with subsequent exposures being reduced by a constant factor, either 1/3 or 1/2. Typical series would thus be 300, 100, 30, 10, 1, ... or 300, 150, 75, 37.5, 18.75, ... nanocoulombs. Fifteen or sixteen exposures are to be made. The 1/2 factor, while slightly more accurate, does not provide the range of detection that the 1/3 factor does. When using the SSMS technique for the analysis of Level 1 samples, all sample component concentrations up to 10 percent (by weight) must be quantified. This will require that those contractors having SSMS spectrometers built for exposure factors of 1/2 will have to prepare two samples for each analysis, a normal sample allowing quantification from the sub-ppm level to several hundred ppm and a second, more dilute sample for quantification up to the 10 percent level.

8.3.1.5 Sample Calculation and Report Forms (See Sections 2.2.7-2.2.9)--

The calculation for an SSMS analysis, even using the disappearing line technique, is moderately complex. An example calculation follows:

- Standardization (Determination of Relative Sensitivity Coefficients)

To determine the relative sensitivity coefficients as discussed in Section 8.3.1.3, the following equation is to be used:

$$S_R = \frac{1}{C_i} \cdot \frac{E_s}{E_i} \cdot \frac{V_s C_s}{\text{wt. sample}} \cdot \frac{A_s}{A_i} \cdot \frac{W_i}{W_s} \cdot \frac{M_i}{M_s}$$

S_R = the experimentally determined relative sensitivity coefficient to correct for other factors that bring about differences in elemental sensitivity.

E_s = the estimate of the maximum exposure at which an isotope of the internal standard present in known concentration "just disappears."

E_x = the similar estimate of the exposure for an isotope of the element of interest in the standard mixture.

V_sC_s = the product of the volume and stock concentration of the internal standard "spike."

wt. sample = the weight of the sample used in preparing the set of electrodes.

A_s/A_x = the ratio of the isotopic abundances of the internal standard isotope to the isotope of interest.

W_x/W_s = the ratio of the line widths of the mass of interest to that of the internal standard; this is approximated in practice by $\sqrt{M_x/M_s}$.

M_x/M_s = the ratio of the mass of interest to that of the internal standard, to convert from atomic concentration to weight concentration.

To simplify a repetitive calculation, the various correction and conversion factors may be regrouped in the following manner:

$$F_1 = \frac{A_s}{A_i} \cdot \sqrt{\frac{M_i}{M_s}} \cdot \frac{M_i}{M_s}$$, the elemental isotope dependent factors.

$$F_2 = \frac{1}{C_i} \cdot \frac{V_sC_s}{\text{wt. sample}} \cdot \frac{E_s}{E_i}$$, the sample-dependent factors.

F_1 = can be calculated and tabulated for each isotope that is used for analysis.

F_2 = is calculated for each sample

As a sample calculation, assume one is to determine S_R for $^{59}Co^+$ relative to $^{166}Er^+$. The data are:

C_i = 10 µg/g

V_sC_s = (1 mL)(100 µg/mL) = 100 µg

wt. sample = 0.0500 g (@ 10 µg/g)

E_i = 0.90 nC (est.)

E_s = 0.082 nC (est.)

$$F_1 = \frac{33.4\%}{100\%} \cdot \sqrt{\frac{59}{166}} \cdot \frac{59}{166} = 0.0708$$

$$F_2 = \frac{1}{10\ \mu g/g} \cdot \frac{100\ \mu g}{0.0500\ g} \cdot \frac{0.082}{0.90} = 18.2.$$

then,

$$S_R = (18.2)(0.0708) = 1.29.$$

- Analysis of an Unknown

The equation used to determine S_R is now rearranged to determine C_i; that is,

$$C_i = \frac{E_s}{E_i} \cdot \frac{V_s C_s}{\text{wt. sample}} \cdot \frac{A_s}{Ai} \cdot \sqrt{\frac{M_i}{Ms}} \cdot \frac{M_i}{Ms}$$

Examples of completed SSMS forms are included as Figures 23, 24, and 25.

8.3.2 Atomic Absorption Spectrometry (refs. 88, 89)

While SSMS can theoretically be used to analyze any element, it has been found that fairly volatile species such as Hg are poorly analyzed by SSMS. Thus, Hg will be analyzed using atomic absorption spectrometry (AAS) (see Figures 20 and 21). AAS will also be used to analyze for Sb and As in the second and third impinger solutions taken from the SASS train; these, plus Hg, are the only species of interest in this sample and using SSMS for just two metals would be inefficient.

8.3.2.1 Mercury Analysis (ref. 90)--

The cold vapor mercury analysis procedure described here is applicable for Level 1 determination of Hg in hydrogen peroxide and ammonium persulfate impinger solutions, bulk liquids, dilute HNO_3 solutions resulting from the Parr bomb combustion of fuels, and aqua regia solutions from the digestion of particulates. The detection limit is 0.04 µg/L when using a 50-mL sample.

The cold vapor mercury analysis is based on the reduction of mercury species in acid solution with stannous chloride and the subsequent sparging of elemental mercury, with nitrogen, through a quartz cell where its absorption at 253.7 nm is monitored. Details of the procedure are provided in Appendix F.

8.3.2.2 Arsenic Analysis (ref. 90)--

Arsenic analysis by AAS is applicable for Level 1 analysis of impinger solutions. The detection limit for the procedure is 0.05 µg with a calculated sensitivity of 0.03 µg per 1 percent absorption.

The analysis procedure involves the reduction and conversion of arsenic to its hydride through a reaction with fresh sodium borohydride (<4 h old). The volatile hydride is swept from the reaction vessel, in a stream of

SSMS ANALYSIS SHEET

Contractor John Doe Engineering

Sample Site Acme Power Station **Sample Acquisition Date** 11/2/78

Type of Source Stack

Test Number 1 **Sample ID Number** APS-JDE-11/2/78-510

Sample Description 3 and 10 μm cyclone catch combination

Analyst Responsible I. M. Accurette **Date Analyzed** 12/15/78 **Time** 9:00

Calculations and Report Reviewed By J. Doe **Report Date** 2/8/79

Instrument MR7 **Resolution** 3000

Sequential Exposure Factor 1/3 **Carbon Type Used for Electrode Preparation** Ultra-1-V-USP

Description of Multielement Calibration Standard Spex Mix

Internal Standard(s) indium

Original Sample Volume or Mass 2 gm

Dilution Factor 1/2 (50 mg carbon/50 mg particulate)

Brief Description of Electrode Preparation Mix sample, graphite, and internal standard. Dry and press into 3-electrode set.

Figure 23. SSMS analysis sheet.

Element		Relative Sensitivity Coefficient	Concentration of Calibration Standard
Uranium		0.69	10 ppm
Thorium		0.65	10 ppm
Bismuth		0.95	10 ppm
Lead		0.98	10 ppm
Thallium		1.41	10 ppm
Mercury			
Gold			
Platinum			
Iridium			
Osmium			
Rhenium			
Tungsten			
Tantalum			
Hafnium			
Lutecium			
Ytterbium			
Thulium			
Erbium			
Holmium			
Dysprosium			
Terbium			
Gadolinium			
Europium			
Samarium			
Neodymium			
Praseodymium			

Element		Relative Sensitivity Coefficient	Concentration of Calibration Standard
Cerium			
Lanthanum			
Barium			
Cesium			
Iodine			
Tellurium			
Antimony			
Tin			
Indium			
Cadmium			
Silver			
Palladium			
Rhodium			
Ruthenium			
Molybdenum			
Niobium			
Zirconium			
Yttrium			
Strontium			
Rubidium			
Bromine			
Selenium			
Arsenic			
Germanium			
Gallium			
Zinc			

Element		Relative Sensitivity Coefficient	Concentration of Calibration Standard
Copper			
Nickel			
Cobalt			
Iron			
Manganese			
Chromium			
Vanadium			
Titanium			
Scandium			
Calcium			
Potassium			
Chlorine			
Sulphur			
Phosphorus			
Silicon			
Aluminum			
Magnesium			
Sodium			
Fluorine			
Oxygen			
Nitrogen			
Carbon			
Boron			
Beryllium			
Lithium			
Hydrogen			

Figure 24. SSMS report – standardization results. (Note that this form is only partially completed, but that it is to be completed in toto during an actual analysis.)

Element	Line Used for Estimate (mass number)	Uncorrected Sample Value	Blank Value	Corrected Sample Value	Assigned Concentration*	At Source Mass/Volume mg/m^3 or µg/L	Detection Limit
Uranium	238	3.4	ND	3.4	3.4	0.0002 mg/m^3	1
Thorium	232	2.6	ND	2.6	2.6	0.0002 mg/m^3	1
Bismuth	207	ND	ND	ND	ND	ND	0.7
Lead	208	68.7	3.4	65.3	65.3	0.004 mg/m^3	1
Thallium	205	2.3	ND	2.3	2.3	0.0001 mg/m^3	0.6
Mercury	NC	NC	NC	NC	NC	NC	18
Gold							
Platinum							
Iridium							
Osmium							
Rhenium							
Tungsten							
Tantalum							
Hafnium							
Lutecium							
Ytterbium							
Thulium							
Erbium							
Holmium							
Dysprosium							
Terbium							
Gadolinium							
Europium							
Samarium							
Neodymium							
Praseodymium							

NOTE THAT THIS FORM IS ONLY PARTIALLY COMPLETED, BUT THAT IT IS TO BE COMPLETED IN TOTO DURING ACTUAL ANALYSIS.

*Results: µg/g (in original sample) or I - interference; NC - not computed; NG - sample value below blank; ND - not detectable (<2σ blank or baseline).

Figure 25. SSMS report—test sample results. (Note that Test Sample Results report forms for the elements cerium through hydrogen are not included here but are included in Appendix A.)

argon, into an argon-hydrogen flame of an atomic absorption spectrophotometer. There the hydride is decomposed and its concentration monitored at the resonance wavelength 193.7 nm. Further details of the procedure are provided in Appendix F.

8.3.2.3 Antimony Analysis (ref. 90)--

Antimony analysis by AAS is applicable for the analysis of ammonium persulfate solutions obtained from Level 1 samples. The detection limit for the procedure is 0.05 µg when using a 10-mL sample.

Organic antimony-containing compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the sample to fumes of sulfur trioxide. The antimony liberated, together with the inorganic antimony originally present, is subsequently reacted with potassium iodide and stannous chloride and finally with sodium borohydride to form stibine. The stibine is removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame in an atomic absorption spectrophotometer. The gas sample absorption is measured at 217.6 nm. Since the stibine is freed from the original sample matrix, interferences in the flame are minimized. Further details are provided in Appendix F.

8.3.2.4 Sample Calculation and Report Forms (see Sections 2.2.7-2.2.9)--

The procedures for determination of Hg, Sb, and As are similar. In each case, the total metal content of an aliquot of sample is transported by a carrier gas into the AAS. The calculation procedures are nearly identical and are illustrated below:

Standard Solutions

Standard Solution No.	Concentration of aliquot	Absorbance*
1	C_{s1}	A_{s1}
2	C_{s2}	A_{s2}
3	C_{s3}	A_{s3}

Blank Solution

Absorbance*
A_b

---

*A double beam spectrophotometer is to be used, thus instrumental background signal is subtracted automatically.

Unknown Solution

Absorbance*

A_u,measured

From a linear regression analysis of the standards' data,

$A_{s,i}$ = (Line Slope) × ($C_{s,i}$) + (Intercept).

Calculate values of C_{blank} and $C_{u,measured}$ from the standard calibration equation, and correct C_u for blank, i.e.,

$C_{u,corrected} = C_{u,measured} - C_b$.

The method for Sb analysis is not very reproducible; therefore a "check" standard must be prepared with each set of samples, compared with the standard curve, and an appropriate correction made. That is,

$$Sb\ (conc) = A \times \frac{B}{C}$$

where

A = concentration of Sb in sample aliquot as determined from calibration equation

B = known concentration of "check" standard

C = concentration of "check" standard as determined from calibration equation.

A typical report form for AAS analysis is given as Figure 26.

8.4 ION CHROMATOGRAPHY (refs. 91-94)

Ion chromatography is a new technique for the analysis of low levels of both cationic and anionic species. It is a multielement technique with a wide dynamic response range, 10 ppb to 1,000 ppm. Because it is so new, the principles of the technique will be summarized here. An ion chromatograph has three principal components: a first column for separation of the ions, a second column for removal of the excess reagent used to elute the ions from the first column, and a conductance cell and bridge for ion detection. For anion separation, the first column would typically be an analytical

---

*A double beam spectrophotometer is to be used, thus instrumental background signal is subtracted automatically.

AAS ANALYSIS SHEET

Contractor John Doe Engineering

Sample Site Acme Power Station **Sample Acquisition Date** 11/2/78

Type of Source Stack

Test Number 1 **Sample ID Number** APS-JDE-11/2/78-110

Sample Description Combined SASS Train Impinger Solutions

Original Sample Volume or Mass 1.00L

Analyst Responsible I. M. Accurette **Date Analyzed** 12/2/78 **Time** 4:00

Calculations and Report Reviewed By J. Doe **Report Date** 2/8/79

	As	Hg	Sb
Instrument Used	PE 603	PE 603	PE 603
Wavelength Setting (nm)	194	254	218
Lamp Current (ma)	8 watts (EDL)	6	8 watts (EDL)
Fuel/Oxidizer Pressures (psi)	H_2/Ar-8/30	-	H_2/Ar-8/30
PM Voltage (volts)	800	800	800
Detection Limit (μg)	0.2	.003	0.1
Sensitivity (abs. units/ppm/ sample volume)	0.2/0.013/20	0.2/0.007/100	0.2/0.025/20
High/Low Calibration Standards (ppm)	.005/.020	.001/.010	.001/.015
Sample Aliquot Volume (mL)	25	25	100
Dilution Factor	1/2	none	none
Uncorrected Sample Aliquot Value (ppm)	0.015	0.002	0.003
Blank Value (ppm)	0.006	0.002	0.000
Corrected Sample Aliquot Value (ppm)	0.009	-	0.003
Assigned Concentration*	0.018	ND	0.003
At Source Mass/Volume, mg/m^3 or μg/L	0.0006 mg/m^3	ND	0.0001 mg/m^3

***Results: PPM value (in original sample) or I - interference; NC - not computed; NG - sample value below blank; ND - not detectable (<2σ blank or baseline).**

Figure 26. AAS analysis sheet.

anion exchange column. The anions would be eluted from this column using a buffered weak base, e.g., $NaHCO_3$, Na_2CO_3. The second column would contain strong cation exchange resin in the H^+ form, which would neutralize the eluting base. The substance eluting from this second column then is the alkali metal-anion salt in a neutral or weakly ionized media. The conductance detector responds only to these salts and the output from the conductance bridge is taken as the analytical signal. The advantages of this method are that it allows multielement (or multispecies) detection and that it is fast, simple, and sensitive.

8.4.1 Sample Analysis

In the Level 1 assessment, IC is to be used for determination of F^-, Cl^-, NO_3^-, NO_2^-, $SO_3^=$, $SO_4^=$, and $PO_4^\equiv$ in bulk aqueous liquids and also in the solution resulting from the aqueous extraction of bulk solids.

A 4-L solution of distilled, deionized water containing 0.5 g each of $NaHCO_3$ and Na_2CO_3 is used as the eluent (i.e., 0.125 g/L). The sample is first filtered and then injected into a sample loop (typically 1 to 2 mL must be injected; 0.1 mL to fill the sample loop and the remainder to fill the tubing leading to the sample loop). A pump rate of approximately 1.5 mL/min (300-400 psig) is used. The anions elute in the following order: F^-, Cl^-, NO_2^-, NO_3^-, $PO_4^\equiv$, $SO_3^=$, and $SO_4^=$. (Br^- will also elute if present.) The anions of interest are then determined by either the method of standard additions or by use of a calibration curve. The method of standard additions should be used whenever the presence of interferences is suspected. These include polyvalent cations such as Fe^{+3} and Al^{+3}, which interfere by forming complexes with F^-; and iron, which will interfere with $PO_4^\equiv$ and CL^- through complex formation.

As a final note and as stated previously, the type of commercial test kit discussed in Chapter 6 may be used rather than IC for determination of these ions if permitted by the EPA project officer.

8.4.2 Sample Calculation and Report Forms (see Sections 2.2.7-2.2.9)

The calculation for ion chromatographic analysis is straightforward as the following example shows.

Standardization:

Standard solution no.	Concentration	Peak height
1	C_{s1}	P_{s1}
2	C_{s2}	P_{s2}
3	C_{s3}	P_{s3}

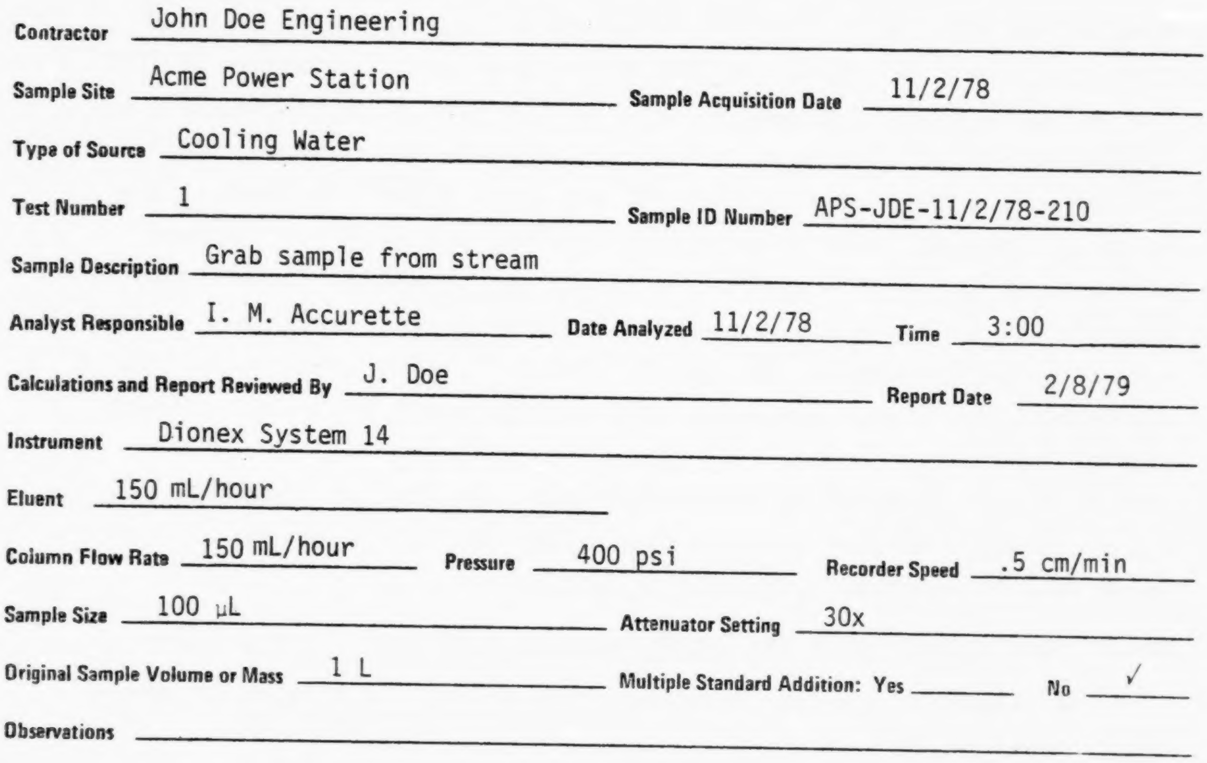
A linear regression analysis of these data yields the standard calibration equation

$$P_{s,i} = \text{(Line Slope)} \times (C_{s,i}) + \text{(Intercept)}.$$

The peak height for an unknown, P_u, is measured as well as that of a blank, P_b. Concentrations $C_{u,\text{measured}}$ and C_b are calculated using the standard calibration equation and $C_{u,\text{corrected}}$ is calculated as

$$C_{u,\text{corrected}} = C_{u,\text{measured}} - C_b.$$

Typical report forms for IC analysis are given in Figures 27 and 28.



Contractor John Doe Engineering

Sample Site Acme Power Station **Sample Acquisition Date** 11/2/78

Type of Source Cooling Water

Test Number 1 **Sample ID Number** APS-JDE-11/2/78-210

Sample Description Grab sample from stream

Analyst Responsible I. M. Accurette **Date Analyzed** 11/2/78 **Time** 3:00

Calculations and Report Reviewed By J. Doe **Report Date** 2/8/79

Instrument Dionex System 14

Eluent 150 mL/hour

Column Flow Rate 150 mL/hour **Pressure** 400 psi **Recorder Speed** .5 cm/min

Sample Size 100 μL **Attenuator Setting** 30x

Original Sample Volume or Mass 1 L **Multiple Standard Addition: Yes** ____ **No** ✓

Observations ____

Figure 27. IC analysis sheet.

Ion	Uncorrected Sample Value	Blank Value	Corrected Sample Value	High/Low Calibration Standards or Concentration Added	Dilution Factor	Assigned Concentration*	Detection Limit*
F^-	0.03	0.03	-	0.1/10	None	ND	0.05
Cl^-	6.8	0.7	6.1	0.1/10	1/10	61	0.07
Br^-	0.6	0.6	-	0.5/10	None	ND	0.5
NO_2^-	0.7	0.7	-	0.5/10	None	ND	0.5
NO_3^-	0.8	0.1	0.7	0.1/10	None	0.7	0.3
$SO_3^=$	1.8	0.7	1.1	0.5/10	None	1.1	0.5
$SO_4^=$	5.6	1.5	4.1	0.1/10	None	4.1	0.1
$PO_4^{\equiv}$	4.2	0.4	3.8	0.5/10	None	3.8	0.2

*Results: µg/L values (in original sample or I – Interference; MC – major constituent, not quantified; NC – not computed; NG – sample value below blank; ND – not detectable ($< 2\ \sigma$ blank or baseline).

Figure 28. IC report—standardization and test sample results.

CHAPTER 9

LEVEL 1 ORGANIC ANALYSIS TECHNIQUES

9.1 INTRODUCTION

The objective of Level 1 organic analysis is to identify the major classes of organic compounds present in a process or effluent stream and to estimate their concentrations. An example of the kind of information the methodology is designed to provide is given in Table 14.

Samples obtained in accordance with the procedures outlined in Chapters 3 through 7 will be either gases, liquids, or solids. The multimedia analysis flow scheme presented in Figure 29 shows how each of the sample types is split for organic analysis.

In Level 1 organic analysis, quantitative information is provided by gas chromatography (total chromatographable organics--TCO) and by gravimetry (GRAV). Qualitative and semiquantitative information is obtained from liquid chromatography fractionation, from infrared spectra, and from low resolution mass spectra. In order to achieve a satisfactory characterization of the sample, the analyst must integrate all of these data, as well as any other available information about the source. Knowledge gained from any one part of the analysis scheme (e.g., LC separation) should be used, to the maximum extent possible, in interpreting the results from other parts (e.g., IR or LRMS spectrum). Table 15 summarizes the data expected from individual samples undergoing Level 1 organic analysis.

9.2 LEVEL 1 ORGANIC ANALYSIS METHODOLOGY (ref. 95)

An overview of the methodology to be used for the Level 1 organic analysis is shown in Figure 30. This methodology deals with the preparation of the samples to provide a form suitable for analysis, and with their subsequent analysis.

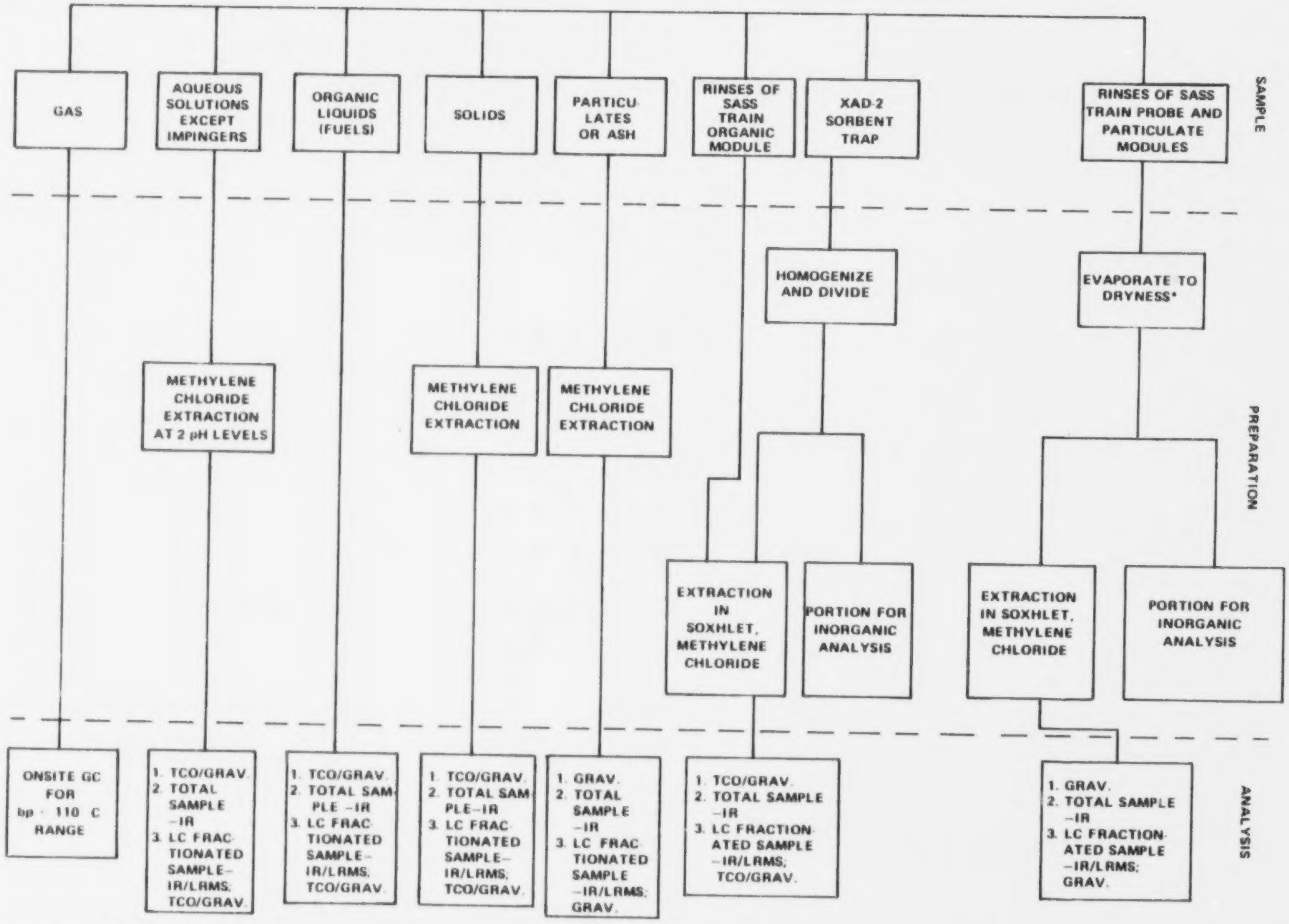
TABLE 14. SUMMARY OF RESULTS FOR ORGANIC EXTRACTS FOR SASS TRAIN SAMPLE

	$\sum$, mg/m^3						
	Particulate module			Sorbent module			
Categories	Rinses*	>3 μm	<3 μm	Resin	Rinse	Condensate†	Total‡
Aliphatic hydrocarbons		<0.06	<0.04	0.3	0.8		1.1
Aromatic hydrocarbons--benzenes				0.6			0.6
Fused aromatics, MW <216		0.25	0.15	6.3	22		29.
Fused aromatics, MW >216		0.25	0.15	4.2	21		26.
Heterocyclic N		0.31	0.19	0.6	19		20.
Heterocyclic S		<0.06	<0.04	0.4	2		2.4
Heterocyclic O		<0.06	<0.04	0.2	2		2.2
Phenols		0.06	0.04	0.1			0.2
Esters		0.18	0.11	0.1	0.1		0.5
Carboxylic acids		<0.06	<0.04	0.3	0.3		0.6
Sulfur					0.2		0.2
Inorganics				0.1			0.1
Unclassified		0.06	<0.04	0.2			0.3
Silicones		0.06	0.04				0.1

*Rinses corresponded to 0.03 mg/m^3 of organics and were not subjected to LC-IR-LRMS analysis.

†No condensate was collected for this sample.

‡Rounded results.


SAMPLE
PREPARATION
ANALYSIS
GAS
AQUEOUS SOLUTIONS EXCEPT IMPINGERS
ORGANIC LIQUIDS (FUELS)
SOLIDS
PARTICULATES OR ASH
RINSES OF SASS TRAIN ORGANIC MODULE
XAD-2 SORBENT TRAP
RINSES OF SASS TRAIN PROBE AND PARTICULATE MODULES
HOMOGENIZE AND DIVIDE
EVAPORATE TO DRYNESS*
METHYLENE CHLORIDE EXTRACTION AT 2 pH LEVELS
METHYLENE CHLORIDE EXTRACTION
METHYLENE CHLORIDE EXTRACTION
EXTRACTION IN SOXHLET, METHYLENE CHLORIDE
PORTION FOR INORGANIC ANALYSIS
EXTRACTION IN SOXHLET, METHYLENE CHLORIDE
PORTION FOR INORGANIC ANALYSIS
ONSITE GC FOR bp < 110 C RANGE
1. TCO/GRAV. 2. TOTAL SAMPLE –IR 3. LC FRACTIONATED SAMPLE– IR/LRMS; TCO/GRAV.
1. TCO/GRAV. 2. TOTAL SAMPLE –IR 3. LC FRACTIONATED SAMPLE– IR/LRMS; TCO/GRAV.
1. TCO/GRAV. 2. TOTAL SAMPLE–IR 3. LC FRACTIONATED SAMPLE– IR/LRMS; TCO/GRAV.
1. GRAV. 2. TOTAL SAMPLE –IR 3. LC FRACTIONATED SAMPLE –IR/LRMS; GRAV.
1. TCO/GRAV. 2. TOTAL SAMPLE –IR 3. LC FRACTIONATED SAMPLE –IR/LRMS; TCO/GRAV.
1. GRAV. 2. TOTAL SAMPLE –IR 3. LC FRACTIONATED SAMPLE –IR/LRMS; GRAV.

*ANALYSIS ENDS HERE IF RESIDUE < 10 PERCENT OF TOTAL PARTICULATE CATCH.

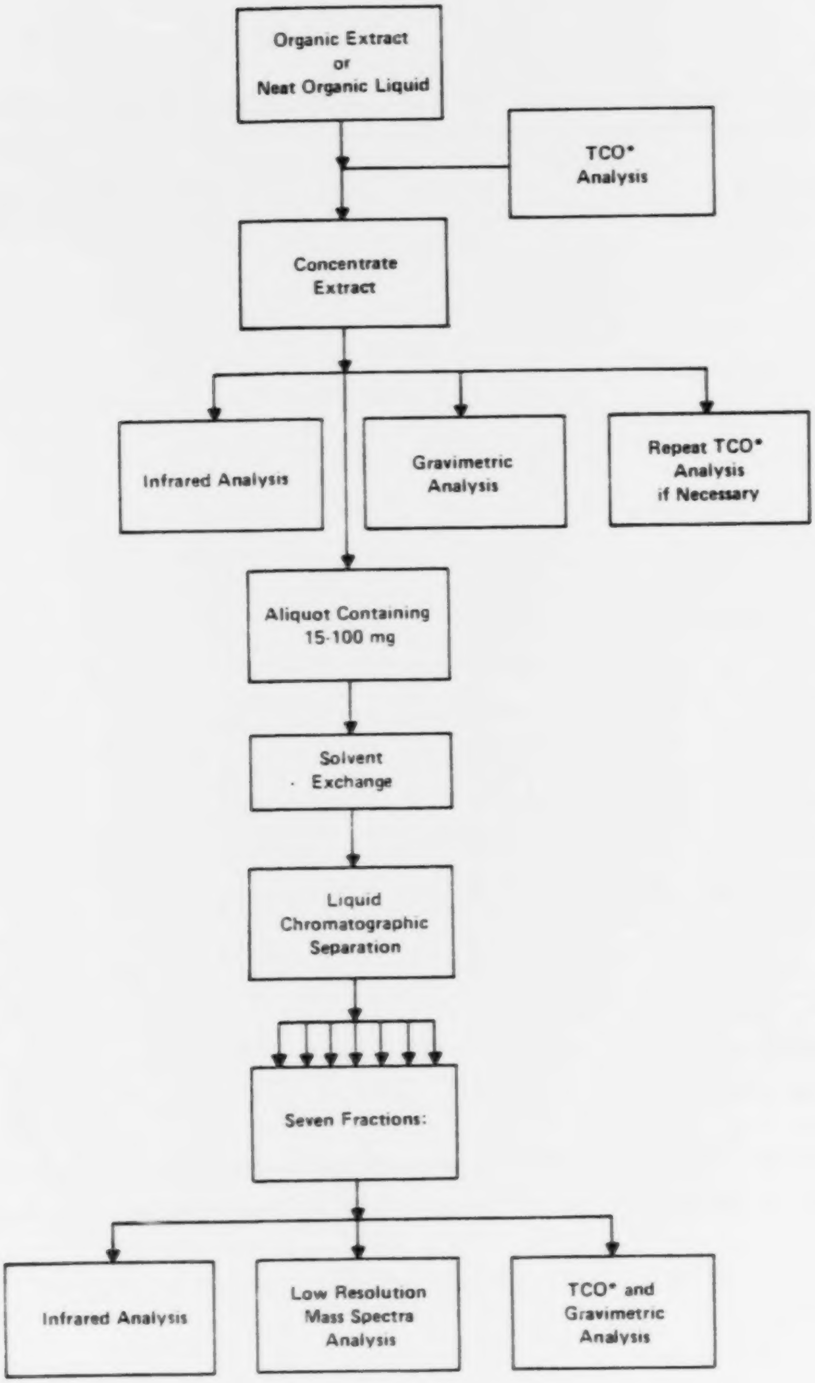
Figure 29. Multimedia organic analysis overview.

TABLE 15. SUMMARY OF EXPECTED DATA FROM LEVEL 1 ORGANIC ANALYSIS

Sample	Onsite GC	Weigh	Extract	TCO	GRAV	IR	LC*
Gases--grab sample	√						
SASS							
>10 µm particulate		√	√		√	√	√
3-10 µm particulate		√					
1-3 µm particulate		√	√		√	√	√
<1 µm particulate		√					
Rinse of particulate modules and probe		√	√†		√†	√†	√†
XAD-2 resin combined with rinse of sorbent module			√	√	√	√	√
Sorbent module condensate			√	√	√	√	√
SOLIDS							
Flyash; clinker		√	√		√	√	√
Organic feed stock		√	√	√	√	√	√
Coal		√	√	√	√	√	√
LIQUIDS							
Effluent water			√	√	√	√	√
Organic feed stock				√	√	√	
Fuels				√	√	√	

*Includes GRAV + IR and TCO on all fractions; perform LRMS when criteria are exceeded.

†Do analysis if gravimetric results are greater than 10 percent of the total particulate catch.


Organic Extract
or
Neat Organic Liquid
TCO*
Analysis
Concentrate
Extract
Infrared Analysis
Gravimetric
Analysis
Repeat TCO*
Analysis
if Necessary
Aliquot Containing
15-100 mg
Solvent
Exchange
Liquid
Chromatographic
Separation
Seven Fractions:
Infrared Analysis
Low Resolution
Mass Spectra
Analysis
TCO* and
Gravimetric
Analysis

*See section 9.4.1.

Figure 30. Organic analysis methodology.

As indicated in Figure 29, the extent of the sample preparation required varies with sample type. The low molecular weight, volatile species (boiling point <100° C) are determined by gas chromatography onsite and require no preparation. Organic liquids, such as fuel oils, will not need pretreatment and are placed directly into the analysis scheme. However, the majority of the samples, including the SASS train components, aqueous solutions such as scrubber waters, and bulk solids such as coal or slag, require extraction with solvent prior to analysis. This extraction separates the organic portion of the samples from the inorganic species. The analysis of organic extracts or organic liquids then proceeds to initial quantitative analyses of volatile (TCO) and nonvolatile (GRAV) organic material and a preliminary infrared (IR) spectral analysis. The IR spectrum provides an indication of the types of functional groups present in the sample and a control checkpoint for subsequent analyses. All functional groups identified in this total sample should be accounted for in the succeeding steps.

The sample extract or organic liquid is separated by silica gel liquid chromatography (LC) using a 7-fraction solvent series of varying polarity. TCO and gravimetric analyses of each fraction are done to determine the distribution of the sample by the various class types. An IR spectrum is then obtained on each LC fraction for determination of the types of functional groups present. Low resolution mass spectra (LRMS) are also obtained on all fractions that exceed the concentration threshold in order to determine the principal compound types present in each fraction. For the sample streams identified in the Level 1 scheme, these threshold concentrations are:

a. Gas streams sampled with the SASS system--0.5 mg/m^3 computed at the source;

b. Aqueous slurry or solid samples--dependent on extract concentration;

c. Organic liquids--1 mg/LC fraction.

The decision is based on the sum of the TCO and GRAV analyses (Section 9.4) for each fraction.

It should be emphasized that sample contamination and solvent impurities are common problems in organic analysis. The best possible laboratory procedures must be used along with verified pure solvents. Blanks and controls are to be run for each stage in the analysis scheme, as specified in Chapter 2.

9.3 PREPARATION OF SAMPLE EXTRACTS

This section presents sample preparation procedures that are appropriate for most samples. The specific solvent indicated for the extraction is methylene chloride, which was selected because of its good solvent properties and high volatility (to facilitate concentration). This solvent should be used except in cases with unusual requirements, for which an alternative procedure can be suggested and used after approval by the project officer and by the Process Measurements Branch, IERL-RTP.

Procedures for concentration and analysis of extracts are presented in Section 9.4.

9.3.1 Aqueous Solutions

Extraction of aqueous solutions should be carried out with methylene chloride using a standard separatory funnel fitted with a Teflon stopcock. The pH of the aqueous phase should be adjusted first to 2.0 ±0.5 with hydrochloric acid and subsequently to 12.0 ±0.5 with sodium hydroxide, using multirange pH paper for indication. Two extractions are to be done at each pH, using a 250-mL volume of methylene chloride for each of the four extractions of a 10-L sample. The extractions may be performed in several batches on convenient-sized sample portions with corresponding amounts of solvent, but the entire 10-L sample must be extracted.

For the SASS train sorbent module condensate, the volume of aqueous solution should be measured and the quantity of methylene chloride adjusted proportionately.

To avoid the necessity of shipping large quantities of water, the extractions should preferably be done onsite whenever facilities will permit contamination-free conditions. If formation of emulsions is encountered, the samples may be shipped to the laboratory for extraction. Centrifugation at about 2,000 rpm has been found to be an effective way to break the emulsion in several studies.

9.3.2 Solids, Particulate Matter, and Ash

All solid material including waste products, raw materials, cyclone, probe and filter particulate, and ash are extracted for 24 h with methylene chloride in a Soxhlet apparatus. When sample quantities are limited, such as in the case of SASS cyclone catches, the designated solid sample aliquots, remaining after a small portion has been set aside for inorganic and particle morphology analysis, should be taken for the extraction. (See Table 11, Chapter 4.) When kilogram quantities of the sample material are available, optimal sample sizes should be used for these determinations. Bulk lumpy solids, such as coal, should be crushed to a size that will pass a 60-mesh screen before extraction, using a procedure such as that in ASTM D 2013, "Preparing Coal Samples for Analysis" (ref. 74). The sample is held in the thimble with a plug of glass wool and a stainless steel screen during the extraction to avoid carryover of the sample.

9.3.3 Slurries and Sludges

The sludge/slurry sample category can span a tremendous range, including slurries and solid or semisolid sludges containing up to 95 percent water. Some of these materials are very difficult to handle and no one procedure will work for all of them. The basic Level 1 approach is to determine whether the sample is best treated as a solid, a liquid, or by a combination of procedures. The protocol will involve, in most cases, tests on small portions of the 1-kg sample to determine the best procedure prior to committing the entire sample. The stepwise protocol follows.

> If the physical character of the sample permits, treat it as a solid by transferring the whole sample to a Soxhlet thimble and extracting for 24 h with methylene chloride. Do not dry sample before extracting. Determine wet weight of sample taken by weighing sample container before and after transferring sample to thimble. If an aqueous phase is noticed in the organic extract, this should be separated and removed prior to concentration.
>
> If the sample state does not appear compatible with direct Soxhlet extraction (i.e., wet sludge/slurry of high liquid content), select a treatment procedure as follows:
>
> 1. Take a 10-mL portion of the sample (shaking vigorously first, if necessary, to facilitate a fairly representa-

tive sampling) and place in a 15-mL centrifuge tube. Add 2 mL methylene chloride. Shake well and allow to settle for at least 30 min. Then:

   a. If sample dissolves completely, treat the sample like a neat organic liquid--no sample preparation is required.

   b. If a clean two-phase (organic-aqueous) separation is achieved, treat the sample like an aqueous sample.

   c. If a clean two-phase separation is not achieved (i.e., if an emulsion forms, or if the apparent solvent recovery is low, or if a three-phase system with solids suspended in organic layer or between organic and aqueous layers is present), centrifuge the mixture. If a clean two-phase system then results, treat sample as in 1.b. above. If not, test sample as suggested in 2., below.

2. Take a 10-mL portion of the sample (shaking vigorously first, if necessary, to facilitate a fairly representative sampling) and place in a 15-mL centrifuge tube. Centrifuge. If phases separate, treat the solid phase by Soxhlet extraction. The liquid phase is treated like an aqueous sample or, if organic, like a neat organic liquid. The several extracts generated for this type of sample should be recombined--taking the same fraction of each--prior to organic analysis.

Occasionally a sludge/slurry sample may be encountered for which none of the above methods will be satisfactory. In those instances, the EPA project officer and appropriate PMB personnel should be consulted for guidance.

9.3.4 SASS Train Rinses

For each SASS train run there are two samples of this type, one from the rinse of the particulate portions (cyclones and filters), and a second from the rinse of the sorbent module. The solvent mixture used for the particulate rinses is 1:1 (v:v) methylene chloride:methanol. This rinse should be dried and weighed. If the residue quantity is greater than 10 percent of total filter and cyclone catch, the full complement of analytical tests should be performed. (See Figure 29.) The rinse for the gas conditioner and sorbent module is methylene chloride alone. It should be added to the Soxhlet solvent reservoir prior to XAD-2 extraction. This will result in a combined rinse and extract characterization for organic compounds. (See Figure 29.)

9.3.5 Sorbent Trap

The XAD-2 resin from the sorbent trap is removed from the SASS train cartridge and homogenized, and a 5-g portion is removed for the inorganic analysis. The balance of the resin is extracted with methylene chloride to remove the organic material. A large Soxhlet extraction apparatus, available from several manufacturers*, must be used to extract the 400 mL of resin. The resin is transferred to a previously cleaned glass extraction thimble†. A glass wool plug and stainless steel screen are used to secure the resin, which would otherwise float on the methylene chloride. Approximately 1 L of methylene chloride is added to the 2-L reflux flask. (The dumping volume of an appropriate commercial extractor is 750 mL.) A larger Soxhlet extractor may be used if available and an appropriate increase in the reflux solvent volume made. The boiling solvent in the flask should be examined periodically because additional methylene chloride may be needed to replace that lost by wetting the resin and by volatilization. The resin is extracted for 24 h. If water is extracted from the XAD-2 resin during this procedure, as evidenced by two phases in the liquid portion, segregate them with a separatory funnel before concentrating the methylene chloride. The aqueous fraction from this separation is added to the condensate catch before it is extracted at the two pH levels.

9.4 ANALYSIS OF SAMPLES FOR ORGANICS

The analysis of each of the prepared or isolated samples for organic compounds follows the scheme introduced in Figure 30. The overall scheme is based upon an initially recommended scheme (ref. 95), which has been revised with information from subsequent laboratory evaluations (ref. 96).

Qualitative analyses of organic compounds are accomplished by the LC/IR/LRMS procedure, which will provide reliable data on the compound types present in the sample or organic extract. However, compounds with boiling points below about 100° C will not be captured in the SASS train or retained in the organic extracts. Consequently, a separate field gas chromatography procedure has been included for the analysis of this range of materials (see Chapter 3), which gives a limited amount of qualitative information (retention times) as well as quantitative information.

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*For example, Ace Glass Incorporated (catalog No. 6810-10) or Lab Glass (catalog No. LG-6910-100).

†Thimbles of borosilicate glass with fritted glass discs must be specially fabricated for this size Soxhlet extractor. Do not use cellulose thimbles.

Quantitative analysis of moderately volatile materials (bp 100° C to 300° C) is achieved by a gas chromatographic procedure applied to various organic solvent extracts, organic liquids, and SASS sorbent module rinses. This Total Chromatographable Organics (TCO, Section 9.4.1) analysis is not appropriate for extracts from samples that do not contain low boiling organics, such as SASS particulate material collected at 200° C. Quantitative analysis of nonvolatile organic sample components (bp >ca. 300° C) in all extracts is achieved by evaporating an aliquot of extract to dryness and weighing the residue (GRAV procedure).

In summary, TCO analyses of extracts and organic liquids are performed prior to any concentration step. It is then necessary to obtain an IR on a portion of this material, to do a gravimetric analysis on an aliquot, and to concentrate the extract for the LC separation. The appropriate stage to conduct each of these steps (gravimetric analysis, IR, concentrate) will depend on the quantity and solubility of the sample as described in the following sections. For many samples, quantitative analyses (TCO and/or GRAV) may be required both before and after concentration.

9.4.1 Total Chromatographable Organics (TCO) Analysis

As previously stated, the TCO analysis is necessary for quantification of materials with boiling points in the range of 100° to 300° C. This analysis is applied to all samples that might contain compounds in this volatility range. These include organic liquids, many solid sample extracts, aqueous sample extracts, extracts from the SASS train sorbent module samples, and LC fractions obtained for those samples. However, particulate samples collected at the specified 205° C SASS train oven temperature or residues from high temperature processes do not require TCO analysis. If, for some special circumstance, the front half of the sampling train is run at a temperature lower than 200° C, then both the TCO and the gravimetric procedures should be applied to the extracts of cyclone particulate catch.

Because materials in the TCO volatility range may be lost to varying degrees during solvent evaporation, it is important that this analysis be performed on extracts and solutions prior to any concentration step. It will also frequently be desirable to repeat the TCO analysis later on the concentrated extract. When the original analysis shows a low TCO value, corresponding to a concentration of less than about 40 mg/L in the extract, the TCO analysis should be repeated on a concentrated extract. This will give a more reliable estimate than that obtained by multiplying the original low concentration estimate by the large volume of unconcentrated extract.

For determination of TCO, a 1- to 5-μL portion of the extract is analyzed by GC using a flame ionization detector. A 1.8 m x 3 mm O.D. (6 ft x 1/8 in.) column of 10 percent OV-101 on 100/120 mesh Supelcoport has been used successfully for this analysis. Other silicone phases (OV-1, etc.) may work as well, but a 10 percent loading is recommended. The GC is operated isothermally at about 30° C--or room temperature--for 6 min after sample injection and then programmed at approximately 20° C/min to 250° C and held at 250° C as long as necessary for complete elution of sample. Injector temperature of 275° C and detector temperature of 300° C are appropriate. Slight modifications in the temperature and duration of the initial hold period may be necessary to accommodate variations in individual GC systems.

Quantitative calibration of the TCO procedure is accomplished by use of mixtures of known concentrations of the normal hydrocarbons C_8, C_{12}, and C_{16}. The quantitative calibration standards should be prepared to cover the concentration range to be studied. Retention time limits corresponding to the TCO range of boiling points are defined by the peak maxima for n-heptane (C_7, bp 98° C) and n-heptadecane (C_{17}, bp 303° C). Therefore, integration of detector response should begin at the retention time of C_7 and terminate at the retention time of C_{17}. By this procedure, the integrated area will cover material in the boiling range of 100° C to 300° C. (The C_7 and C_{17} peaks should not be included in the quantitative calibration.)

In the TCO analyses, it is important that the observed values of total integrated area for samples be corrected by subtracting an appropriate solvent blank prepared (i.e., concentrated) in the same manner as the samples. The blank should be checked on each of the seven LC solvent mixtures.

The results of each TCO analysis should be reported as one number, in milligrams, corresponding to the total quantity of material in the 100° to 300° C boiling range in the original sample collected (see Figure 31). The TCO data are thus analogous to the results obtained by gravimetric analysis. The chromatograms themselves contain some additional data beyond the TCO values (i.e., retention times and areas of individual peaks) and should be retained until the Level 1 sampling and analysis effort has been completed.

9.4.2 Gravimetric (GRAV) Analysis

The gravimetric analysis is used for quantification of organic sample components with boiling points higher than 300° C. This analysis should be done after the sample extract has been concentrated, since it is recommended to weigh at least 10 mg of sample in a gravimetric analysis, when possible. Weighing to a precision of ±0.1 mg is adequate for purposes of Level 1 analysis. Sample and tare weights should be obtained by drying to "constant weight" (±0.1 mg) in a desiccator over silica gel or Drierite. In performing a gravimetric analysis on a large volume sample (i.e., >50 mL), no more than 5 mL of extract should be evaporated to dryness. For extracts concentrated to 10 mL, a 1-mL aliquot is taken for GRAV analysis. The GRAV results should be reported as one number for the entire sample (see Figure 31). The infrared analyses called for in Level 1 organic analysis can be performed on the residues from the GRAV procedure, provided that the weighing dishes were successively rinsed with distilled water, methanol, and methylene chloride before use.

9.4.3 Concentration of Extracts and Solvent Exchange Procedure

After the initial TCO* analysis, it will usually be necessary to concentrate the organic extracts to a volume of 10 mL for subsequent analysis. It is recommended that concentration to slightly less than 10 mL volume (i.e., 8 or 9 mL) be accomplished using a Kuderna-Danish apparatus with a 3-ball Snyder column for volumes less than 1 L, and a rotary evaporator for volumes that initially exceed 1 L. It is essential that the extract not be reduced to dryness at this point in the scheme to prevent loss of TCO range material. The concentrated extract should then be transferred to a convenient graduated container (e.g., Kuderna-Danish receiver or centrifuge tube) and the volume restored to 10 mL. The concentration process should be stopped if material begins to drop out of solution. In that case, the extract should be restored to a convenient volume in which the material is redissolved. The original TCO* analysis may provide guidance as to the degree of concentration that is required for each particular sample. The objective is to achieve a final concentration of not more than 100 mg/mL and a final volume of not less than 10 mL.

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*On all samples except SASS particulate fractions and residues from high temperature processes.

At this stage in the analysis sequence, a GRAV determination is done and the TCO* determination is repeated.† A 1-mL aliquot is used for the GRAV analysis and a 5-μL aliquot is used for the TCO. If the sum of TCO plus GRAV is <15 mg for the total sample, the LC separation is not performed and the Level 1 analysis is concluded by obtaining IR and LRMS spectra on the sample. If the sum of TCO plus GRAV is ≥15 mg, the LC separation is performed. An IR spectrum is also obtained on the residue from the GRAV analysis or on a separate aliquot of extract. A portion of the concentrated extract that contains about 100 mg of organic material, if possible, is taken for the LC. Smaller quantities down to a lower limit of 15 mg may be used if necessary.

The LC separation procedure requires that both methylene chloride solvent and water be eliminated before the sample extract is applied to the silica gel column. Otherwise, the required aliphatic/aromatic and subsequent compound class separations will not be achieved. Extracts that do not contain low boiling organics, such as SASS train particulate materials or other materials collected at temperatures exceeding 200° C (400° F), can be evaporated to dryness with silica gel, as detailed below, before LC analysis.

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*On all samples except SASS particulate fractions and residues from high temperature processes.

†Unless the initial TCO values for the unconcentrated extract exceeded the guideline of 40 mg/L (TCO).

Extracts containing appreciable quantities of TCO material (>2 mg) must be transferred to the LC columns without being evaporated to dryness. For these samples, a solvent exchange procedure is required to minimize losses of volatile sample components. An aliquot of the methylene chloride solution containing 15 mg (minimum) to 100 mg (preferred) of sample is taken for solvent exchange into cyclopentane; the detailed procedure is given below. Normal hydrocarbon solvents are not to be substituted for the cyclopentane; pentane boils too low (36° C, below methylene chloride) and hexane boils too high (68° C) for the solvent exchange. The solvent exchange and removal of water from the sample extracts is accomplished as described in Section 9.4.4.3.

9.4.4 Liquid Chromatographic (LC) Separation

All sample extracts, neat organic liquids, and SASS-train-dried probe/cyclone rinse extracts are subjected to LC separation if sample quantity is adequate. An aliquot of the concentrated extract containing 100 mg of organic matter is preferred for the LC, but smaller quantities down to a lower limit of about 15 mg may be used. The sample components are separated according to polarity on silica gel using a step gradient elution technique. The detailed procedure for the LC separation is given below:

Column:	200 mm x 10.5 mm ID, glass with Teflon stopcock, water-jacketed with inlet water temperature in the range of 18° to 22° C and sufficient flow to maintain this temperature through to the outlet.
Adsorbent:	Davison, Silica Gel, 60-200 mesh, Grade 950 (available from Fisher Scientific Company) is to be used; no other types or grades of silica gel can be substituted. This material should be cleaned prior to use by sequential Soxhlet extractions with methanol, methylene chloride, and pentane. This adsorbent is then activated at 110° C for at least 2 h just prior to use, and cooled in a desiccator.

Drying Agent: Sodium Sulfate (Anhydrous, Reagent Grade). Clean by sequential Soxhlet extraction for 24 h each with methanol, methylene chloride, and pentane. Dry for at least 2 h at 110° C just prior to use and cool in a desiccator.

9.4.4.1 Procedure for Column Preparation--

The chromatographic column, plugged at one end with a small portion of glass wool, should be slurry packed with 6.0 g of freshly activated silica gel in n-pentane. A portion of properly activated silica gel weighing 6.0 ±0.2 g occupies 9 mL in a 10-mL graduated cylinder. The total height of the silica bed in this packed column is 10 cm. The solvent void volume of the column is 2 to 4 mL. When the column is fully prepared, allow the pentane level in the column to drop to the top of the silica bed so that the sample can be loaded for subsequent chromatographic elution.

After packing the silica gel column, add 3 g ±0.2 g clean sodium sulfate to the top of the column. Vibrate for 1 min to compact. The sodium sulfate should occupy 2 mL in a 10-mL graduated cylinder. The sodium sulfate will remove small quantities of water from the organic extract; however, appreciable quantities of water will solidify the sodium sulfate, inhibiting proper flow through the column. Therefore, it is advisable that if enough water is present in the sample to form two layers, it should be removed by another method--pipette or separatory funnel.

9.4.4.2 Evaporation of Sample Extracts with Low TCO (≤2 mg original sample)--

For these samples, the aliquot of extract containing 15 mg (minimum) to 100 mg (preferred) of material is added to a small amount of silica gel, the solvent is allowed to evaporate, and the residue plus silica gel is transferred to the LC column with the aid of a microspatula. The container is rinsed as described in Section 9.4.4.5.

9.4.4.3 Solvent Exchange of Sample Extract with High TCO (>2 mg original sample)--

An aliquot of methylene chloride extract containing 15 mg (minimum) to 100 mg (preferred) of material is added to 200 mg of silica gel in a graduated receiver. The volume of extract is carefully reduced to 1 mL at ambient temperature under a gentle stream of nitrogen (tapped from a liquid nitrogen cylinder, if possible, to minimize impurities). The solvent evaporates rapidly so it is important that this operation be done under constant surveillance to insure that the volume is not reduced below 1 mL. It is also necessary to warm the samples slightly, either by hand or water bath, at ≤40° C, to prevent condensation of atmospheric moisture in the sample due to evaporative cooling. One milliliter of cyclopentane is added and mixed by gentle agitation. The volume is reduced to a total of 1 mL as before. A second milliliter of cyclopentane is added, mixed, and the volume is again reduced to 1 mL. The exchange is repeated with a third milliliter of cyclopentane. After the volume has been reduced to 1 mL for this last time, the solvent mixture will be ≤5 percent methylene chloride. This is sufficiently low to prevent breakthrough of aromatic sample components into the aliphatic hydrocarbon fraction, LC1.

The cyclopentane and silica gel are transferred to the top of the previously prepared LC column using a Pasteur pipette. The container is rinsed as described in Section 9.4.4.5.

9.4.4.4 Neat Organic Liquids--

A 100-mg sample is weighed into a tared glass weighing funnel and mixed with about 200 mg of silica gel using a microspatula. The sample is then transferred to the top of the column. The container is rinsed as described in Section 9.4.4.5.

When neat organic liquids are fractionated by the liquid chromatography scheme, they have the same theoretical gravimetric detection limitations as other samples separated by this means, 0.1 mg/100 mg or 0.1 percent of the sample applied. Since these aliquots are neat samples and do not have concentration factors as multipliers, the resultant detection limits for minor components are 1 g/kg at best.

9.4.4.5 Chromatographic Separation into Seven Fractions--

Table 16 shows the sequence for the chromatographic elution. In order to insure adequate resolution and reproducibility, the column elution rate is maintained at 1 mL/min.

TABLE 16. LIQUID CHROMATOGRAPHY ELUTION SEQUENCE

Fraction	Solvent composition	Volume (mL)
1	Pentane	25
2	20% Methylene chloride in pentane	10
3	50% Methylene chloride in pentane	10
4	Methylene chloride	10
5	5% Methanol in methylene chloride	10
6	20% Methanol in methylene chloride	10
7	50% Methanol in methylene chloride	10

The volume of solvents shown in Table 16 represents the solvent volume added to the column for that fraction. If the volume of solvent collected is less than the volume actually added due to evaporation, restore the fraction volume to the proper level with fresh solvent. In all cases, the solvent level in the column should be at the top of the gel bed, i.e., the sample-containing zone, at the end of the collection of any sample fraction. The fractions are retained as solutions for TCO analyses.

After the first fraction is collected, rinse the original sample container or weighing funnel with a few milliliters of Fraction 2 solvent (20 percent methylene chloride/pentane) and carefully transfer this rinsing into the column. Repeat with each successive solvent mixture in turn.

Add each new solvent to the column slowly to minimize disturbing the gel bed and eliminate the trapped air bubbles, particularly in the zone of the sample-containing silica gel.

After each sample is collected, an aliquot (1 to 5 μL) is taken for TCO analysis of each fraction (unless the sample taken for LC had a TCO of ≤ 2 mg). Also, an aliquot (10 ml for Fraction 1 and 5 mL for Fractions 2-7) is transferred to a tared aluminum micro weighing dish for evaporation and gravimetric analysis. The GRAV data for Fraction 7 must be corrected for a blank contributed by a small quantity of silica gel that dissolves in the highly polar eluent. The blank value is determined by running an LC column to which no sample is added; it is on the order of 0.9 ±0.1 mg in LC7 (10 mL).

After TCO and GRAV determinations, the fractions are analyzed by IR and, when the quantity is sufficient, by LRMS (see Section 9.4.6).

The objective of the LC procedure is to separate the sample into fractions of varying chemical class type to facilitate subsequent analyses. The LC separation procedure is not a high resolution technique and, consequently, there is overlap in class type between many of the fractions. Figure 31 shows a sample LC report with a number of compound classes represented in the eluent.

The results of the LC fractionation procedure include quantitative estimates of TCO and GRAV range materials in each of seven fractions. In most cases, the quantity of material actually taken for the LC separation is only a portion of the total sample, and the amount taken should be stated in the report. The actual, measured TCO and GRAV values for the LC fractions should be multiplied by the appropriate factor (total sample quantity ÷ quantity taken for LC) to give the corresponding total sample values. It is then useful to convert these quantitative estimates into equivalent concentrations at the source in order to facilitate comparisons with various decision criteria. Figure 31 illustrates the format for reporting LC fractionation data, with an example from a SASS train sorbent trap extract. Note that GRAV analyses involve weighing to the nearest 0.1 mg. TCO values are reported to the nearest 0.1 mg, also.

9.4.5 Infrared Analysis

The total sample extract, or neat liquid, and the 7 LC fractions are analyzed by infrared (IR) spectrophotometry. A grating spectrophotometer should be used and the following instrument conditions adhered to.

1. Resolution: For dispersively measured spectra, the spectral slit width should not exceed 4 cm^{-1} through at least 80 percent of the wave number range.
2. Wave number accuracy: ±4 cm^{-1} below 2,000 cm^{-1} and ±15 cm^{-1} above 2,000 cm^{-1}.
3. Noise level: No more than 2 percent peak to peak.
4. Baseline flatness: The I_0 or 100 percent line must be flat to within 5 percent across the recorded spectrum.

LC REPORT

SAMPLE: II-3 SORBENT TRAP EXTRACT

	TCO mg	GRAV mg	TCO + GRAV Total mg	Concentration mg/ (m^3, L, or kg)
Total Sample[1]	106	386	492	82
Taken for LC[2]	23	84	107	18
Recovered[3]	17	74	91	15

Fraction	TCO in mg				GRAV in mg				TCO + GRAV Total mg	Concentration mg/ (m^3,L, or kg)
	Found in Fraction	Blank	Cor-rected	Total[4]	Found in Fraction	Blank	Cor-rected	Total[4]		
1	0.3	0.0	0.3	1.4	2.5	0.0	2.5	11.5	12.9	1.9
2	3.3	0.1	3.2	15.0	1.0	0.1	0.9	4.1	19.1	3.2
3	12.0	0.5	11.5	54.0	56.4	2.5	53.9	247.9	301.9	50.0
4	0.1	0.0	0.1	0.5	2.2	0.1	2.1	9.7	10.2	1.7
5	0.2	0.1	0.1	0.5	6.8	0.5	6.3	29.0	29.5	4.9
6	0.7	0.0	0.7	3.2	3.6	0.2	3.4	15.6	18.8	3.1
7	0.1	0.0	0.1	0.5	0.6	0.0	0.6	2.8	3.3	0.6
Sum	16.7	0.7	16.0	75.1	73.1	3.4	69.7	320.6	395.8	65.9

1. Quantity in entire sample, determined before LC
2. Portion of whole sample used for LC, actual mg
3. Quantity recovered from LC column, actual mg
4. Total mg computed back to total sample

Figure 31. Sample LC report.

5. Energy: The instrument should be purged with dry gas or evacuated so that atmosphere water bands do not exceed the allowable noise level (2 percent) when the instrument is ued in a double beam mode.
6. Spectral range: Spectra should be recorded, without gaps, over the spectral range 3,800-600 cm^{-1}.
7. False radiation: Not to exceed 2 percent.

IR spectra are obtained in absorbance units on samples held between two NaCl salt plates using methylene chloride to transfer the sample to the plates. KBr pellets can also be used if films (from $MeCl_2$) will not give satisfactory spectra, i.e., material is a crystalline solid. Sample quantity and instrument parameters are adjusted so that the maximum signal of the strongest peak is less than 1.0 absorbance.

Spectra are interpreted in terms of functional group types present in the sample or LC fraction. The many reference texts (refs. 96-101) in this area are of considerable help in interpreting the IR spectra. The interpretation of the spectra should also be guided by consideration of the LC fractionation scheme and the LRMS results (when available).

The results of the IR analysis should be reported in the format shown in Figure 32 according to the following guidelines:

a. The frequency reported should be the peak maximum, or a range may be reported instead for broad peaks with no well-defined maximum.
b. Absorbance values should be measured by baseline technique. The intensity is reported relative to the strongest peak in the spectrum on a percentage absorbance basis.
    S = strong, 70-100 percent of the absorbance value of the strongest peak.
    M = medium, 30-70 percent of the absorbance value of the strongest peak.
    W = weak, 0-30 percent of the absorbance value of the strongest peak.

When a peak is of borderline intensity, it should be labeled "m." Finer intensity ratings such as M-S or W-M are not appropriate.

IR REPORT

SAMPLE: II–3–LC6

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3400	M	OH, NH	Broad
3050	W	unsat'd CH	
2850, 2920	M	sat'd CH	
1710	S	acid, ketones	
1680	M	amide, ketones	
1600	M	aromatic C = C	
1450	M	CH_2	
1060	S	Si–O, ether	Broad
740	M	subst. pyridine, C–Cl	

Figure 32. Sample IR report.

c. The assignment/comments column indicates the functional group(s) to which the peak is attributed*. This column may also contain single-word descriptors of peak shape such as "broad," "doublet," "shoulder."

d. All weak, medium, and strong peaks must be reported.

e. A copy of the infrared spectrum should be retained at the laboratory for 3 years should further reference to it be needed.

As a matter of quality control, the IR bands observed with each LC fraction should be compared to those observed with the total sample. Additional bands in any of the fractions would indicate the introduction of impurities or decomposition on the column. The IR bands observed with the total sample but not with any of the LC fractions would indicate loss of material onto the column.

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*All features of the IR spectrum, such as presence or absence of bands at other related IR frequencies, should be considered in making the functional group assignments.

9.4.6 Low Resolution Mass Spectrometry (refs. 102-105)

A low resolution mass spectrum (LRMS) is obtained on each LC fraction that has sufficient quantity (TCO plus GRAV), when referenced back to the source, to exceed decision criteria concentrations. The Process Measurements Branch guidelines recommended for general Level 1 purposes are:

Gas--SASS train samples	0.5 mg/m^3
Ambient air--particulate	1 μg/m^3
Solids	1 mg/kg
Aqueous solutions	0.1 mg/L

An LRMS analysis is to be done on any LC fraction that corresponds to a source concentration higher than these levels.

In the event that other, more stringent criteria are determined to be appropriate for a particular environmental assessment, then the cutoff point for performing LRMS will change accordingly. For example, if MEG/MATE (Multimedia Environmental Goals/Minimum Acute Toxicity Effluent) concentration values are to be used in making Level 1 decisions, then LRMS must be done on all LC fractions for a SASS sample. This is because MATE values are sufficiently low that in each LC fraction there is at least one compound category that might be present whose level of concern would be exceeded by any detectable quantity of material.

In order to minimize the cost of the Level 1 organic analysis, it is desirable to keep the total number of LRMS analyses required as low as possible. An LRMS analysis must always be run on any LC fraction that exceeds the Level 1 concentration criteria given above. However, if the more stringent (MEG/MATE) cutoff criteria are used, it is acceptable, for LRMS purposes only, to combine fractions falling below the Level 1 concentration criteria, according to the following scheme:

LC1 = LRMS-1
LC2 plus LC3 = LRMS-2, 3
LC4 plus LC5 = LRMS-4, 5
LC6 plus LC7 = LRMS-6, 7

This will allow LRMS results to be obtained on all LC fractions in a minimum number of separate LRMS analyses. The IR data obtained with each LC fraction should be considered before making the decision to combine fractions. If the IR spectra of two fractions considered for combination are vastly different, those fractions should probably not be combined as the LRMS of the mixture will be especially difficult to interpret.

The mass spectrometer used in this determination should have a resolution ($\bar{M}/\Delta M$) of 800 to 1,000, batch and direct probe inlet, variable ionizing voltage source, and electron multiplier detection. Samples with significant quantities of TCO range material (>2 mg) should be analyzed by insertion in the batch inlet. All samples that meet the decision criteria for quantity (TCO plus GRAV) will require analysis via the direct insertion probe. A small quantity of sample is placed in the probe capillary and inserted into a cool source. The temperature is then programmed up to vaporize the sample. Spectra are recorded periodically through this period. Spectra are normally obtained at 70 eV ionizing voltage, but low voltage (10 eV) spectra may provide much simpler data and thus aid in interpretation in some cases.

The mass spectroscopist should integrate the interpretation of the batch and probe mass spectra obtained on a particular sample to provide one report describing sample chemistry. Details of quantitation of LRMS data are too numerous to be addressed in this manual.

Interpretation of the mass spectra is guided by knowledge of the LC separation scheme, the IR spectra, and other information about the source. In reporting the results of the LRMS analysis, the basic philosophy is to present increasingly more specific data as the complexity (or simplicity) of the spectra will allow. The first level of reporting is to identify compound classes. If possible, or appropriate, one should then attempt to identify the subcategory compound classes present in the fraction. Finally, specific compounds should be identified, if possible to do so from the spectra. Where possible, the molecular weight range and composition of each category should be estimated with a rating of 100 = major, 10 = minor, and 1 = trace.

It should be possible, using this methodology, to account for nearly all observed species by selection from a relatively small list of compound categories and subcategories. A tentative list of such categories has been assembled in Table 17. The primary reference for selecting these categories was the MEG list, which seems to do an adequate job of representing all probable major compound classes. Some few categories were not in the MEG list and have been added here.

TABLE 17. CATEGORIES FOR REPORTING LRMS DATA

Category (Subcategory)	Most probable LC fraction*	Category (Subcategory)	Most probable LC fraction*
Aliphatic hydrocarbons	1	Phenols	6
(Alkanes)	1	(Alkyl, etc.)	6
(Alkenes)	1	(Halogenated phenols)	6
(Alkynes)	1	(Nitrophenols)	6
Halogenated aliphatics	1,2	Esters	6
(Saturated)	1,2	(Phthalates)	6
(Unsaturated)	1,2	Ketones	6
		Amines	6
Aromatic hydrocarbons	2,3	(Primary, secondary, tertiary)	6
(Benzenes)	2,3	(Hydrazines, azo compounds)	6
Halogenated aromatic hydrocarbons	2,3	(Nitrosoamines)	6
Nitro aromatic hydrocarbons	4,5		
		Heterocyclic nitrogen compounds	
Fused alternate, nonalternate hydrocarbons	2,3	(Indoles, carbazoles)	4
MW < 216 (methyl pyrene)	2,3	(Quinolines, acridines)	6
MW > 216	2,3		
		Alkyl sulfur compounds	6
Ethers	4	(Mercaptans)	6
(Halogenated ethers)	4	(Sulfides, disulfides)	6
Epoxides	4	Heterocyclic sulfur compounds	
		(Benzothiophenes)	4
Aldehydes	4		
Heterocyclic oxygen compounds	3,4	Sulfonic acids, sulfoxides	7
Nitriles	4	Amides	6
(Aliphatic)	4		
(Aromatic)	4		
		Carboxylic acids	6,7
Alcohols	6		
(Primary, secondary, tertiary)	6	Silicones	2,3,4
(Glycols)	6		
		Phosphates	5,6,7

*Possible assignments. Fractions 4-5, 5-6, 6-7 generally overlap to a considerable extent. Also, additional components of a particular molecule may cause it to elute in an LC fraction other than that expected. For example, a short-chain ester would probably elute in LC fraction 5 or 6 whereas a long-chain ester would elute in Fractions 3 or 4.

The list in Table 17 is also organized somewhat differently than the MEG list to be more compatible with the nature of the mass spectrometry data. It should be strongly emphasized that the list probably does not include all identifiable compound categories. If interpretation of the spectra yields the identification of a category not included in this table, the category should be reported. At the same time, EPA/PMB should be notified of the need to add that category to the list. It will be possible in most cases to identify the spectra in terms of the compound categories listed in Table 17, but one should avoid force fits if another category seems more appropriate.

Interpretation of the mass spectral data should take full advantage of all other information known about the sample source, i.e., LC fraction and IR spectra. Since the LC separation does a reasonable job of dividing compound classes, the categories listed in Table 17 have been listed in order of their possible elution from the LC column. Where possible, some indication has been made as to the LC fraction in which the category might elute. These fraction assignments are known to be correct in some cases and are only estimates in others. Sometimes the sample characteristics will have minor effects on the fraction elution behavior. Again, the LC fraction indications should only be taken as a guideline. Figure 33 gives a completed example of a reporting format for the LRMS data. Blank forms may be found in Appendix A.

It is once again emphasized that interpretation of the LRMS data is best done using all available information, such as what one knows about the chemistry of the source being sampled, what species generally elute in the LC fraction being examined, and functional group data derived from the IR spectra.

9.5 ORGANIC ANALYSIS SUMMARY TABLES

At the end of the Level 1 organic analysis procedure, there will be an LC report, seven IR reports, and up to seven LRMS reports for each organic extract or neat organic sample. This is an unwieldy body of data from which to make a decision. The first step in reducing these data to a workable form is to prepare a single table that summarizes the organic analysis

LRMS REPORT

SAMPLE: II-3-LC6

Major Categories

Intensity	Category	MW Range
100	Ketones	180-280
100	Heterocyclic Nitrogen Compounds	167-253
10	Esters	
10	Carboxylic Acids	
10	Phenols	

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	Acridine	179	$C_{13}H_9N$
100	Fluorenone	180	$C_{13}H_8O$
10	Phenol	94	C_6H_6O
10	Cresol	108	C_7H_8O
10	Benzoic Acid	122	$C_7H_6O_2$
10	Carbazole	167	$C_{12}H_9N$
10	Methylacridine	193	$C_{14}H_{11}N$
10	Methylfluorenone	194	$C_{14}H_{10}O$
10	Anthraquinoline	229	$C_{17}H_{11}N$
10	Benzanthrone	230	$C_{17}H_{10}O$
10	Dibenzofluorenone	280	$C_{21}H_{12}O$
10	Dibutylphthalate	278	$C_{16}H_{22}O_4$
10	Methylbenzanthrone	244	$C_{18}H_{12}O$

Other

Figure 33. Sample LRMS report.

results for each extract. Figure 34 illustrates the organization of this table and the following paragraphs describe the various entries.

Space is allotted in the table heading for a sample identification code. It is assumed that each laboratory will have devised its own coding system (see Chapter 2) for uniquely identifying the various samples. It may be desirable to include the date, the name of the analyst, or other similar information.

The body of the table includes one column for each of the LC fractions and one column for summing the data. The first set of data entries is the quantitative analysis, transcribed from the LC report. The calculated total organic loading corresponding to each fraction is entered in the first row. This value is used in estimating the abundance of the various organic compound classes. The next two rows contain the estimated TCO and GRAV values to indicate the distribution of total volatile (bp 100°-300° C) and nonvolatile (bp >300° C) organic materials. This information can be useful later in the selection of appropriate decision criteria (Level 1, MATE, etc.) values for comparison with the Level 1 results. The results of the compound category analysis (primarily from LRMS data) are summarized in the bottom columns.

For those LC fractions that contained sufficient quantity to have been analyzed by LRMS, the results of the LRMS analyses are summarized in the table as follows: The major categories present in LC fraction 1 are listed at the left-hand side of the table and the approximate intensity (100, 10, or 1) for each category is entered in the LC1 column. To convert the LRMS intensity index to a concentration estimate for each organic compound category, the individual intensity value is divided by the sum of all intensities for the LC fraction and then multiplied by the total organic loading (mg/m^3) estimated for the fraction. This procedure is then repeated for the other LC fractions. Examples are worked in Figure 35 for two LC fractions, LC2 and LC4, of the same XAD-2 extract.

The results presented in Figure 34 illustrate the considerable overlap in chemical class composition that can be expected between some fractions in the Level 1 LC scheme. As noted earlier, this is not a high resolution separation technique and the various compound categories cannot be uniquely

ORGANIC EXTRACT SUMMARY TABLE

Sample Sorbent Extract–II-3

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg	18.2	22.3	253	29.7	11.0	46.3	15.1	390
TCO, mg	5.2	19.	73.	6.7	3.7	5.3	0.1	110
GRAV, mg	13.	3.3	180.	23.	7.3	41.	15.	280

Category	Assigned intensity--mg/___(m³, L, or kg)*							
Sulfur	100–0.6							0.6
Aliphatic HC's	10–0.06							0.06
Aromatics–Benzenes		10–0.06						0.06
Fused Arom 216		100–0.6	100–4	100–0.5				5.
Fused Arom 216		10–0.06	100–4	100–0.5				5.
Heterocyclic S		10–0.06	10–0.4	10–0.05				0.5
Heterocyclic N				10–0.05	–0.1†	100–0.7	10–0.02	1.
					–0.1†	10–0.07	100–0.2	0.3
Carboxylic Acids					–0.1†	100–0.7	10–0.02	1.0
Phenols					–0.01†	10–0.07	10–0.02	0.1
Esters					–0.01†	10–0.07		0.08

*Concentration for gas samples = mg/m^3, for liquid samples = mg/L, for solid samples = mg/kg. Fill in actual m^3, L, or kg value.

†Estimated assuming same relative intensities as LC6, since IR spectra of LC5 and LC6 are very similar.

Figure 34. Organic extract summary table.

LC 2

Total organics = 0.57 mg/m^3

Aromatic HC's-benzenes	10
Fused Arom <216 MW	100
Fused Arom >216 MW	10
Heteroyclic S Compounds	10

LC 4

Total organics = 6.6 mg/m^3

Fused Arom <216 MW	100
Fused Arom >216 MW	100
Heterocyclic S Compounds	10
Heterocyclic O Compounds	10

Calculation of Concentration Estimates by Category

$\sum$ intensities = 130

Aromatic HC's - benzene: $\frac{10}{130} \times 0.57 = 0.04$ mg/m^3

Fused Arom <216 MW: $\frac{100}{130} \times 0.57 = 0.4$ mg/m^3

Fused Arom >216 MW: $\frac{10}{130} \times 0.57 = 0.04$ mg/m^3

Heterocyclic S Cmpds: $\frac{10}{130} \times 0.57 = 0.04$ mg/m^3

$\sum$ intensities = 220

Fused Arom <216 MW: $\frac{100}{220} \times 6.6 = 3$ mg/m^3

Fused Arom >216 MW: $\frac{100}{220} \times 6.6 = 3$ mg/m^3

Heterocyclic S Cmpds: $\frac{10}{220} \times 6.6 = 0.3$ mg/m^3

Heterocyclic O Cmpds: $\frac{10}{220} \times 6.6 = 0.3$ mg/m^3

Figure 35. Sample calculations of concentration estimates from LRMS data.

assigned to particular LC fractions. The data do show the expected trend, in that LC2 is relatively richer in light aromatics (benzene and fused species with MW <216) than is LC4. The fact that adjacent LC fractions can be expected to show gradual changes in chemistry can serve as a useful guide for the analyst in detecting contamination. Very abrupt changes in apparent composition or the appearance of a compound class in an entirely unexpected fraction (i.e., phthalates in LC2 or paraffins in LC6) should be regarded with suspicion.

The overlap between fractions can also be used in estimating the composition of those fractions that did not contain sufficient material to trigger an LRMS analysis. For any LC fraction that was not analyzed by LRMS, it is suggested that the IR spectrum be compared with the IR's of the adjacent fractions. If a close correlation is found between two IR spectra, then this, together with the known behavior of the LC scheme, suggests that the two LC fractions have similar, though not identical, qualitative composition. It is therefore suggested that the total organics in the non-LRMS LC fraction be distributed over the same classes and in the same proportion as was done for the adjacent LC fraction whose IR spectrum was the best match. The error introduced by this procedure into the overall description of sample chemistry will be small, since only fractions with small amounts of material are excluded from the LRMS.

Concentrations estimated by this procedure should be identified with an asterisk in the organic extract summary table and an explanatory footnote should be included.

For those LC fractions for which only IR data are available, the procedure for estimating concentrations by compound class is as follows:

1. List all categories from Table 17 that could be in that fraction.
2. Assign a weighting factor of 100 to each category that appears to be present in the sample based on the IR spectrum.
3. Assign a weighting factor of 10 to each category for which functional groups were not identified.

Then, in the absence of evidence to the contrary, assume that categories with an intensity of 100 may constitute up to 50 percent of the total sample and those with an intensity of 10 up to 10 percent. Clearly, this procedure may "account for" more than 100 percent of the total sample. However, this conservative method of estimation seems necessary because it is not always possible to determine from the IR spectrum of a mixture alone how the various functional groups are assembled into molecules or classes.

Table 18 illustrates this procedure for an LC5 sample, assuming only IR and LC data were available. Concentrations estimated on the basis of IR and LC data only should be footnoted with a dagger in the organic extract summary table and an explanatory footnote should be included.

Once concentrations have been estimated for all compound categories identified in the seven LC fractions for a particular organic extract, or neat organic liquid, these values are summed across each row of the table. (See Figure 34.) This procedure condenses the information obtained on the various LC fractions to provide an integrated description of the chemical composition. In the case of liquid and solid samples, the summation column represents the total concentration/compound category information for the stream sampled. For gaseous streams, the summary report for each component of the SASS train must be added to determine the stream composition, as was shown in Table 15.

9.6 QUALITY CONTROL IN LEVEL 1 ORGANIC ANALYSIS

This discussion has been written for the analytical chemist, who can be presumed to be familiar with generally accepted standards of good laboratory practice. It is worthwhile, however, to reemphasize the importance of some procedures, in addition to sample preparation and analysis per se, which have a very significant impact on the overall quality of the analytical results. Some of those procedures, in particular those related to preventing and/or recognizing sample contamination, are especially critical in a Level 1 environmental assessment.

To insure adequate data quality, it is essential that blanks (controls) be analyzed along with the samples, as discussed in Chapter 2. There is no reliable way to identify spurious results and/or sample contamination other than by finding the same contaminant in a control sample.

TABLE 18. ESTIMATION OF FRACTION COMPOSITION FROM IR AND LC DATA ONLY

Sample LC 5 IR Report Wave number cm^{-1}	I	Assignments/comments	Total Organics = 0.28 mg/m^3		Estimated possible concentration (mg/m^3)*
			Categories most probable in LC 5	Assigned weighting factor	
3,400	S	OH or NH (broad)	Heterocyclic N compounds	100	0.14
3,050	M	Aromatic CH	Heterocyclic S compounds	10	0.03
2,850-2,950	S	Aliphatic CH	Sulfides, disulfides	10	0.03
2,230	M	C≡N or C≡C, cyanates or isocyanates	Nitriles	100	0.14
			Ethers	100	0.14
1,700	S	Ketone, carboxylic acid, aldehydes	Aldehydes, ketones	100	0.14
1,600	S	Conj. C=C or aromatic C=N, N-NO_2, C-N=O, Carboxylate	Nitroaliphatics	100	0.14
			Alcohols	100	0.14
			Nitroaromatics	100	0.14
1,530	M	C=N, C-NO_2	Amines	100	0.14
1,420-1,450	S	CH_3, NH_4^+, CH_2, Si-phenyl carbonates	Phenols	100	0.14
1,050-1,300	M	Alcohol C-O, phenol C-O, ether C-O, C-F, various P-O compounds, various Si-O or Si-C compounds	Esters	10	0.03
700-850	S	Subst. benzene rings, some olefinic C-H, C-Cl, CF-CF, some peroxides			

*Total organics = 0.28 mg/m^3.

Control sample, of course, means more than a simple reagent blank for the analysis itself. The control sample and its handling throughout the laboratory sequence should be identical to the real sample and <ins>its</ins> handling, except that the real sample has been exposed to a process stream in a sampling procedure. For instance, an unexposed XAD-2 cartridge must be dumped, homogenized, and a 5-g aliquot reserved for the Parr bomb ashing and trace element assays. The remainder must be Soxhlet extracted and the extract subjected to the entire organics analysis sequence.

The procedures for cleaning the XAD-2 resin prior to use are specified in Appendix B. The quality control checks described in the appendix should be applied to each batch of resin before it is used in a field study.

Each lot of organic solvent (i.e., each new batch number) must be checked for contamination. A volume of solvent equivalent to that used in sample extraction should be evaporated to dryness. The residue should be weighed and examined by IR. If any significant quantity of organic contamination is found, the solvent batch must be redistilled or rejected entirely. Solvents used should be Burdick and Jackson "distilled in glass" or equivalent quality. Note that use of chemicals of the specified grade does not eliminate the necessity of performing checks on the quality of each new batch of material used. However, use of high-quality reagents is important to minimize the probability of acquiring unsatisfactory lots of material, which would require repurification or replacement. Sodium sulfate and silica gel used in the LC separation will frequently require cleanup by extraction with organic solvent prior to use, as described in Section 9.4.4.

These controls and blanks should permit the analyst to identify the source of any background contaminant and to make corrections to the results of sample analyses. If contamination is excessive (more than 10 percent of the sample level), the source should be traced and the contamination eliminated, if possible. Note that silicones (from lubricants/sealants) and phthalates (from plastics) are major potential interferences and must be avoided entirely in collection, storage, and handling of samples for organic analysis.

CHAPTER 10

PARTICULATE MORPHOLOGY AND CLASSIFICATION

10.1 INTRODUCTION (refs. 71, 106-113)

The solid samples taken in Level 1 environmental assessment studies (fly ash, SASS samples, fugitive emissions, slags, etc.) have physical properties that are extremely useful in classifying their origins and/or assisting in evaluating their pollution potential. These physical properties are readily determined by personnel trained in using basic light and polarized light microscopy techniques. For example, a photomicrograph of glassy spheres from combustion source effluent material suggests the presence of inorganic matter transformed at high temperature. Information on the refractive index, size, and inclusions further defines the probable material. Similarly, fugitive emission catches may be compared with feed stock materials and the various particulate process effluents for a good idea of the type and source of these emissions.

10.2 HANDLING PARTICULATES FOR MICROSCOPIC EXAMINATION

Since analytical determinations are actually made on nanogram quantities of the material, care must be taken to avoid introducing contamination during sample procurement, handling, storage, and preparation. For large solid samples, such as slags and coals, a representative portion must be chipped and ground to a fine powder prior to the examination. A description of all size reduction procedures must accompany any particulate characterization. Conversely, for solid samples of fine particulate matter such as SASS cyclone catches, fly ash, etc., care must be taken to avoid crushing or grinding the individual particles prior to examination. For suspended solids in liquid, microscopic examination may be performed on the neat sample and on evaporated deposits on a slide.

10.3 EQUIPMENT SPECIFICATIONS

Adequate observations of particles may be made using any of a variety of good compound microscopes with the following minimum requirements. The microscope must have strain-free achromatic lenses with a numerical aperture rating for the objective lens of less than 1/100 × the total system magnification. Objective lens magnifications of X10 and X43 are sufficient while that of the ocular should be X10 or greater. The microscope should have a uniform illumination source. Polarized light microscopy must be performed using an instrument with a rotating stage having a marked scale or substage polarizer and analyzer lenses. All combinations of lenses and camera attachments should be calibrated for dimensional analysis with an ocular graticule or scaler and an etched stage micrometer.

10.4 MOUNTING OF SAMPLE MATERIALS

Sample mounting techniques have a great influence on the appearance of the sample materials being viewed. There are three procedures that shall be used to examine a solid sample. The first is dry mounting, which provides the least chance for introducing artifacts into the preparation and the best condition for observing true reflected light. Deposit about a milligram of well-mixed sample and spread it about the center of the slide with a needle in concentric motion. The ideal area coverage of the material in the microscope field would be about 5 percent. View the slide without a coverslip. The particles should be separated, not clumped or aggregated.

A second mounting procedure entails mixing the sample with a drop of high refractive index (RI) mounting material such as Canada balsam (RI = 1.535). This may allow better definition of shape and size.

The third mount is the microscopist's choice. He or she may choose to blank out certain particles or background interference by using a mounting medium with a refractive index that is within 0.002 of that material. Thus, a quartz fiber filter with a 1.460 RI will be rendered optically transparent when mounted in a medium with a similar index of refraction. All other material with a higher or lower RI will be visible when it is trapped on the filter. Given different sample types, the mounting media would be chosen to accentuate other special features.

A fresh preparation should be made for analytical determinations since sample changes, such as aggregations, color change, etc., may occur over time in prepared material. Permanently mounted preparations should be kept on file for future reference along with any photograph locator coordinates to specific fields.

10.5 SAMPLE VIEWING

Mounted samples should first be viewed under low power (i.e., with 4-10X stereoscope) followed by higher magnification for general orientation and to determine the samples' particulate types and size classes. The next step involves a description of each specific type of particle present and an estimate of its abundance as a percentage of the total material present. This description should include shape, preliminary sizing (range), color of transmitted light, color of reflected light (if available), surface features, morphology, aggregation, transparency, cleavage, etc. A summary sheet as shown on page A-46 should report all aspects of each particle type along with a definition of the viewing system used in examining the sample. Any questionable determinations should be noted with qualifying comments to alert the reader to the possibility of alternate interpretations. The analyst should make any other observational comments secondary to the above requested class characterization information. Other comments might include a tentative particle identification if accompanied by supportive evidence. The primary objective again is to achieve particle classification and characterization with secondary emphasis on identification. Level 2 investigation will provide more detailed size analysis and positive particulate identification.

10.6 GRAPHIC ILLUSTRATIONS

Photomicrographs of the three sample preparations provide good documentation of sample characteristics and should be included in the particle description report. High contrast black and white film may be used for shape definition and enumeration. Color film (polaroid or photomicrographic) is required for polarized light photomicrographs and can also be used for the other micrographs. Provide a tick mark as a scaler on prints, i.e., 1 μm = ├──┤. In all instances, the mounting and viewing specifications must be included to provide background for the graphic interpretation.

CHAPTER 11

BIOLOGICAL ASSESSMENT

11.1 INTRODUCTION

A principal role of the Industrial Environmental Research Laboratory in environmental protection is to assure that the types and levels of industrial emissions that are regulated are limited to those that might prove harmful to ecology or health. One of the most effective means of providing this information is through direct biological testing of the industrial process emissions for their toxic, mutagenic, or other adverse effects upon sensitive organisms and test systems. Biotesting has not been developed to the extent of being an absolute criterion for site clearance or for establishing regulatory status. Rather, these procedures complement the chemical and physical investigations in the Level 1 phased approach by providing a selective, biologically integrated appraisal of complex sample reactions with various test systems. The combined information from the respective areas of investigation--physical, chemical, and biological--will permit a rational identification of sources of greatest environmental concern. From this information base, further testing or control activities can be effectively planned.

The following discussion outlines the principles of the biological testing procedures. Result report forms for the various biological tests are included in Appendix A of this manual to further illustrate the nature of the Level 1 biological assessment. Additional forms and details of the procedures are found in the IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests for Pilot Studies, EPA 600/7-77-043 (ref. 114) and its revisions. Testing must be performed in approved laboratory facilities by qualified and experienced professionals adhering to strict quality control measures. Samples must be tested as soon after being taken as possible.

11.2 SAMPLING

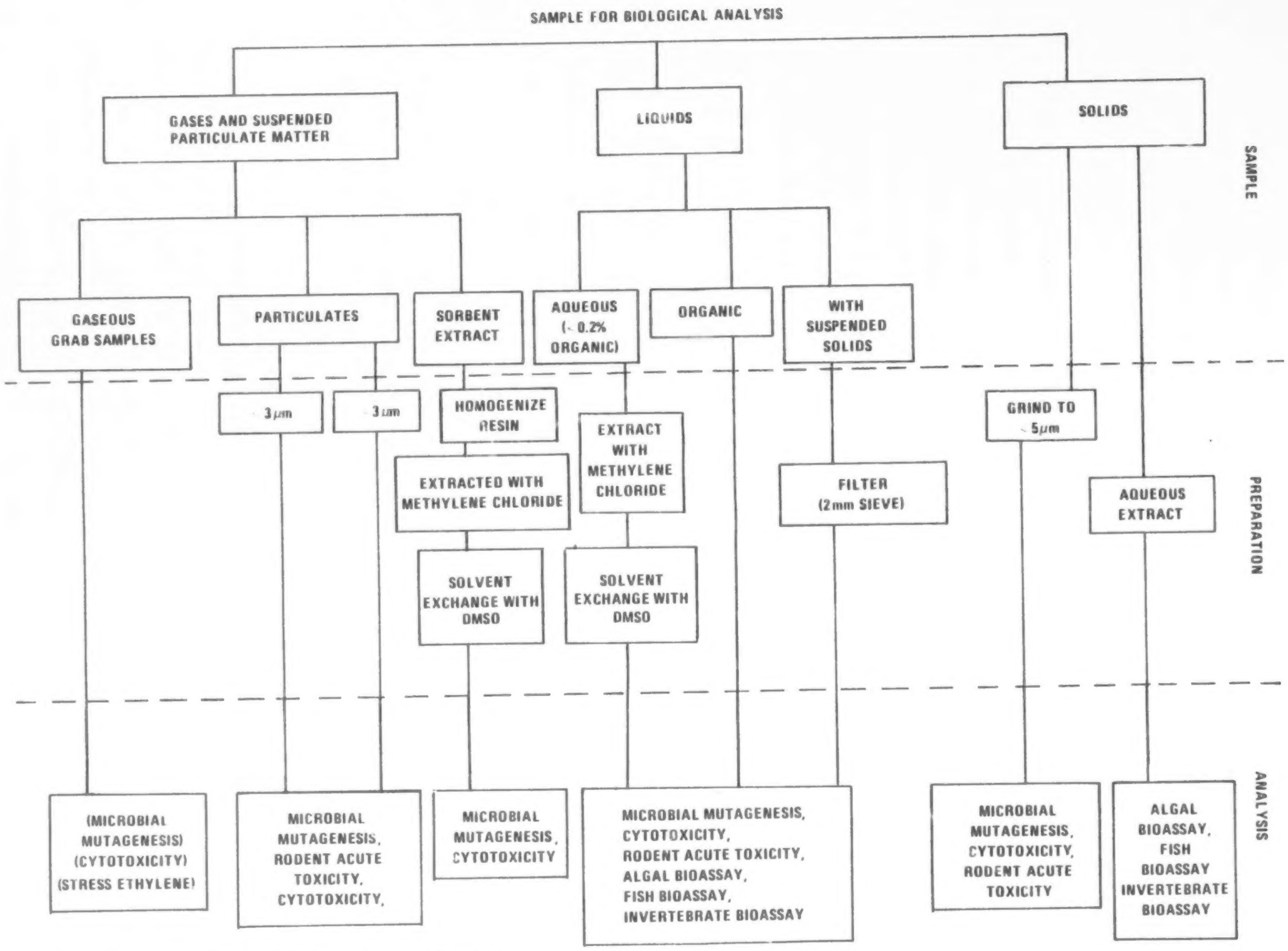
Biological testing for environmental assessment Level 1 purposes involves a survey technique using extract and whole sample incorporation of representative solids, liquids, or gaseous discharges. The diverse sample types and selective test systems used in their characterization are summarized in Figure 36. General guidelines for sampling and sample handling are presented in the biological test manual and in the preceding chapters of this manual. Precise instructions for obtaining samples and performing testing cannot be produced to cover every circumstance encountered in environmental assessment testing; however, sampling methods used for acquisition of samples presented in this manual are usually sufficient.

The following brief descriptions outline the various testing methods applicable to the Level 1 environmental assessment survey. Selections of appropriate test types for particular samples obtained must be made with the combined guidance of the project officer and the biological procedures manual. The interpretation of test results will be the responsibility of the biological committee until such time as guidelines for this activity are published. Results from the bioassays will be reported according to the format explained in the biological procedures manual.

11.3 HEALTH EFFECTS TESTS

11.3.1 Salmonella/Microsome Mutagenesis Assay (Ames) (refs. 115-118)

The Ames test will be used as a primary screen to determine the mutagenic potential of complex mixtures or component fractions. It has recently been demonstrated that most carcinogens act as mutagens. The Ames Assay is based on the property of selected *Salmonella typhimurium* mutants to revert from a histidine-requiring state to prototrophy due to exposure to various classes of mutagens. The test can detect nanogram quantities of mutagens. It has also been adapted to mimic some mammalian metabolic processes by the addition of aryl hydrocarbon hydroxylase activity from a mammalian liver 9,000 G microsomal fraction (S-9). In extensive testing, the Ames assay has demonstrated 90 percent accuracy in detecting known carcinogens as mutagens. Certain known carcinogens are negative (e.g., asbestos and metals) or weakly positive in the test. False positive results are also known--substances


SAMPLE FOR BIOLOGICAL ANALYSIS
SAMPLE
PREPARATION
ANALYSIS
GASES AND SUSPENDED PARTICULATE MATTER
LIQUIDS
SOLIDS
GASEOUS GRAB SAMPLES
PARTICULATES
SORBENT EXTRACT
AQUEOUS (< 0.2% ORGANIC)
ORGANIC
WITH SUSPENDED SOLIDS
3 μm
3 μm
HOMOGENIZE RESIN
EXTRACTED WITH METHYLENE CHLORIDE
SOLVENT EXCHANGE WITH DMSO
EXTRACT WITH METHYLENE CHLORIDE
SOLVENT EXCHANGE WITH DMSO
FILTER (2mm SIEVE)
GRIND TO < 5μm
AQUEOUS EXTRACT
(MICROBIAL MUTAGENESIS) (CYTOTOXICITY) (STRESS ETHYLENE)
MICROBIAL MUTAGENESIS, RODENT ACUTE TOXICITY, CYTOTOXICITY,
MICROBIAL MUTAGENESIS, CYTOTOXICITY
MICROBIAL MUTAGENESIS, CYTOTOXICITY, RODENT ACUTE TOXICITY, ALGAL BIOASSAY, FISH BIOASSAY, INVERTEBRATE BIOASSAY
MICROBIAL MUTAGENESIS, CYTOTOXICITY, RODENT ACUTE TOXICITY
ALGAL BIOASSAY, FISH BIOASSAY INVERTEBRATE BIOASSAY

NOTE: BIOLOGICAL TESTS SHOWN IN PARENTHESES ARE OPTIONAL.

Figure 36. Biological analysis overview.

that are mutagenic in the Ames system but are noncarcinogenic in mammals. Continued improvement of the present bacterial strains, addition of new strains, and reevaluation of the conventional animal carcinogenesis data are expected to reduce this level of test error even further in the near future.

11.3.2 Clonal Toxicity Assay

In some cases, a toxicity assay is employed for comparative purposes utilizing an appropriate cell type, e.g., CHO cells. This technique involves the plating of a specified number of cells per tissue culture dish, generally 100 to 1,000 in increments of 100. Following cell attachment, replicate plates are exposed to particulate or soluble (aqueous or limited organic) toxicants for 24 to 48 h. The cultures are then washed free of toxicant, resupplied with fresh growth medium, and allowed to develop discrete "clonal" colonies of cells. After 10 to 16 days (time depends upon the cell line), the cultures are fixed, stained, and counted.

11.3.3 Cytotoxicity Assays

Cytotoxicity assays employ mammalian cells in culture to quantitatively measure the cellular metabolic impairment and death resulting from in vitro exposure to soluble and particulate toxicants. Mammalian cells derived from various tissues and organs can be maintained as short-term primary cultures or, in some cases, as continuous cell strains or lines. The cytotoxicity assays, available as part of Level 1 analysis, employ primary cultures of rabbit alveolar (lung) macrophages (RAM) and maintenance cultures of strain WI-38 human lung fibroblasts. The alveolar macrophage constitutes an essential first line of pulmonary defense by virtue of its ability to engulf and remove particulate materials that are deposited in the deep lung. It is appropriate, therefore, that this cell type be used to define the acute cellular toxicity of airborne particulates and associated chemicals. It has been possible to "rank" the toxic response to a series of industrial particulates collected on a cyclone sampling train similar to the SASS train (ref. 6). The strain WI-38 human lung fibroblasts are perhaps the best characterized diploid human cells available for cytotoxicity screening. These cells exhibit the major pathways of DNA, RNA, and protein synthesis common to all dividing cells and can be shown to possess a number of inducible enzyme systems.

11.3.4 Acute In-Vivo Test in Rodents

Since the major objective of the Level 1 biological testing procedure is to identify toxicology problems at minimal cost, it is recommended that a two-step approach be taken to the initial, in vivo toxicological evaluation of unknown compounds. The first is based on the quantal (all-or-none) response of 10 rats to a single 10-g/kg dose administered by gavage. Toxicological effects are also noted over the following 14-day period. Normally, the quantal test is used to determine the necessity to carry out the quantitative assay. Should one or more of these test animals die or exhibit gross toxic effects in this experiment, a second, more extensive test involving a quantitative (graded) response may be performed. In this series, 80 rats are divided into groups, each of which receives a fraction of the original dose. LD_{50} and other toxicological information is again noted over the following 14 days.

11.4 AQUATIC ECOLOGICAL EFFECTS TEST

11.4.1 Freshwater Algal Assay Procedure: Bottle Test

An algal assay is based on the principle that growth is limited by the nutrient that is present in shortest supply with respect to the needs of the organism. The test is designed to be used to quantify the biological response (algal growth) to changes in concentrations of nutrients and to determine whether or not various effluents are toxic or inhibitory to algae. These measurements are made by adding a selected test alga to the test water and determining algal growth at appropriate intervals.

11.4.2 Bioassay with Unicellular Marine Algae

The community of unicellular algae is a very important constituent of marine ecosystems because of the photosynthetic production of most of the food and oxygen used by other members of the community. It is comprised of a variety of species that have different growth rates, photosynthetic rates, nutrient requirements, etc. Thus, relevant environmental parameters regulate species composition and diversity.

This sensitivity to environmental changes is used as a test index. Species may be inhibited or stimulated by pollutants. In a community, a pollutant may affect some species but not others, thereby causing changes in species diversity and composition. This can be followed by changes in composition of the animal community and altered routes of flow of energy and materials. Often, the altered ecosystem is undesirable from the human standpoint. In this test, selected marine algae species, such as *Skeletonema costatum*, are exposed to waters or contaminants in question and the growth response is monitored.

11.4.3 Acute Static Bioassays with Freshwater Fish and Daphnia

The fathead minnow (*Pimephales promelus*) is the primary vertebrate used in all tests carried out under this protocol for the environmental assessment studies. The invertebrate choice is *Daphnia magna*, which should be used if additional toxicity data are desired or if it is impossible to use the fathead minnow. These representative aquatic organisms will integrate synergistic and antagonistic effects of all the components in the aqueous test sample over the duration of their exposure. The test is scored by the number of dead or affected organisms after a specified period, i.e., every 24 h after the beginning of the test. More frequent observations may be desirable, especially at the beginning of the test.

11.4.4 Static Bioassays with Marine Animals

The method recommended for static bioassays on marine animals uses juvenile sheepshead minnows (*Cyprinodon variegatus*) and adult grass shrimp (*Palaemonetes pugio* or *P. vulgaris*) as the test species. These species adapt easily to a wide range of salinity and temperature in static bioassays. This method has proven satisfactory for ranking industrial effluents relative to their toxicity to other marine animals.

11.5 TERRESTRIAL ECOLOGY TESTS

Terrestrial bioassays have been developed relatively recently, and show great promise in evaluating complex industrial effluents. These techniques are under review by IERL-EPA, and their current status is subject to change. Interested parties should contact the PMB staff of IERL or refer to the latest edition of the Level 1 Biological Tests Manual if there are questions.

11.5.1 Stress Ethylene/Foliar Injury Plant Response

This test is based on the well-known plant response to environmental stress that involves the release of elevated levels of ethylene. Under normal conditions, plants produce low levels of ethylene. By exposing plants to various levels of gaseous effluents and subsequently quantitating the ethylene released relative to the control conditions, the stress ethylene release attributable to the effluent can be determined in a graded response.

11.5.2 Seed Germination/Seedling Growth Test

These tests allow evaluation of toxic chemicals from environmental samples that are inhibitory to seed germination and root elongation. The tests are well documented for pure compounds and have been validated for use by the Office of Toxic Substances. The tests are particularly suited for aqueous effluents and aqueous leachates from solid samples. The test evaluates the effect of a sample on a variety of seed species; its advantages are that it is short-term, inexpensive, and requires minimum space for testing.

11.5.3 Soil Respiration/Nitrogen Fixation Test

This combination of tests can be performed on any solid or liquid waste material and is particularly applicable to material destined for overland distribution or for landfill operations. The test is based on changes in normal respiration of CO_2 by general microbial activity of a soil sample and general ability of microbes to take up nitrogen surrogates. Soil respiration and nitrogen fixation are classic tests best suited to detecting the severe effects of toxic insults to soils.

11.5.4 Insect Bioassays

The objective of the insect bioassays being considered is to measure the acute toxicity of a solid, liquid, or gaseous sample on sensitive insect species. Two insect species are being considered for Level 1 biological testing, the honeybee and the fruitfly. The advantages of insect tests are their relative low cost, short-term analysis time, and small sample size requirements.

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APPENDIX A

DATA SUMMARY FORMS

PRETEST SITE SURVEY

I. GENERAL

Date of Survey ______________________

Company Name ______________________

Address ______________________

____

Telephone ______________________ SIC Number ______________________

- -

CONTACTS

Name	Title	Telephone

- -

Process ______________________

____

____

Batch ______________________ or Continuous ______________________

Operating Schedule ______________________

____

____

Best Time to Test ______________________

Signature Required on Passes ______________________ Waivers ______________________

Description of Pollution Control Equipment and Operation ______________________

____

____

____

- -

MOTELS

Name	Location	Rate	Telephone

Restaurants Available ______________________

____

Airport ______________________ Distance to Plant ______________________

SITE MAP

II. SAMPLING

A. Sample Type to be Collected:*

1. Raw Materials ______________________
2. Product ______________________
3. Make-Up Water ______________________
4. Fuel ______________________
5. Process Stream ______________________
6. Scrubber Water ______________________
7. Ash ______________________
8. Water Effluent ______________________
9. Airborne Fugitive ______________________
10. Surface Fugitive ______________________
11. Control Equipment Effluent ______________________
12. Other ______________________

Individual Sample Points:

a. Description: ______________________

____

Location: ______________________

____

How to Sample: ______________________

____

b. Description: ______________________

____

Location: ______________________

____

How to Sample: ______________________

____

c. Description: ______________________

____

Location: ______________________

____

How to Sample: ______________________

____

d. Description: ______________________

____

Location: ______________________

____

How to Sample: ______________________

____

e. Description: ______________________

____

Location: ______________________

____

How to Sample: ______________________

____

f. Description: ______________________

____

Location: ______________________

____

How to Sample: ______________________

____

*Check type to be collected. Stack effluent described under Individual Sample Description.

B. Stack Effluent

1. Stack Data

Properties of Sampling Locations	Stack #1	Stack #2	Stack #3	Stack #4
Purpose of stack				
Height ft.				
Width ft. (Top/Bottom)				
Length ft.				
Diameter at port ft., I.D.				
Wall thickness in.				
Material of construction				
Existing Ports: a. Size opening b. Distance from platform				
Straight distance before port Type of restriction				
Straight distance after port Type of restriction				
Environment				
Work space				
Ambient temperature °F				
Average pitot reading, H_2O, in inches				
Approximate stack velocity ft/min.				
Approximate std flow, ft^3/min.				
Approximate moisture % by volume				
Approximate stack temperature °F				
Approximate particulate loading gr/SCF				
Approximate particle size				
Approximate composition gases present				
Approximate stack pressure H_2O, in inches				
Water sprays				
Approximate dilution air				
Elevator				

2. Sketch of stack to be sampled showing locations of port opening, water sprayers, flow interferences, dilution air inlets, and scaffolding or platform erection dimensions. Attach photograph if available.

III. SUPPORT MATERIALS

A. Available at Plant

1. Parking facilities ______________________
2. Electrical extension cords ______________________
3. Electrician ______________________
4. Ice ______________________
5. Weighing balance ______________________
6. Cleanup area ______________________
7. Laboratory facilities ______________________
8. Scaffolding ______________________
9. Restroom ______________________
10. Rope ______________________

B. Electricity Sources

1. Number of circuits* ______________________
2. Amperage per circuit* ______________________
3. Location of fuse box ______________________
____
4. Extension cord lengths ______________________ Quantity ______________________
5. Adaptors needed ______________________

C. To be Purchased or Rented

1. Ice
   Location ______________________ Telephone ______________________
2. Scaffolding
   Height ______________________ Size ______________________
   Vendor ______________________
   Address ______________________
   Telephone ______________________

---

* Two 30-A circuits or four 15-A circuits are required to operate the SASS train.

IV. SAFETY CHECKLIST

A. Medical:

1. **Plant first aid available (yes/no)** ______________ .
   If available give location of unit and telephone number.
   ____
2. **Phone number for ambulance:** ______________________
3. **Phone number for hospital:** ______________________
4. **Comments:** ______________________
   ____

B. Test Site Checklist *(Check if OK)*

1. **Ladders:**
   General conditions ______________ **Rest stops** ______________ **Cage** __________
   Comments: ______________________
   ____
2. **Scaffolds/Platforms:**
   General conditions ______________ **Guardrails** ______________
   Toeboards ______________ **Screening** ______________
   Comments: ______________________
   ____

C. Personnel Protection Equipment *(check if needed)*:

1. **Safety glasses** ______________ **Side shields** ______________
   Face shields ______________ **Goggles** ______________ **Hard hat** __________
   Safety shoes ______________ **Electrical hazard shoes** ______________
   Life belt and safety block __________ **Hearing protective devices** __________ **Ladder climbing devices** __________
2. **Respiratory equipment:**
   Air purifying ______________ **Air supplied** ______________ **Self-contained** ______________
   Other ______________________
   ____
3. **Body protection:**
   Chemical protection garments ______________________
   Heat protective garments ______________________
   Chemical gloves ______________________
   Heat resistant gloves ______________________
   Other ______________________
   ____

D. Are Fire Extinguishers Available at Site __________ ?

E. Special or Unusual Test Procedures and Safety Precautions Necessary:

____
____
____

ORGANIC COMPOUNDS (bp < 100° C)

Contractor ____________________

Sample Site ____________________ **Sample Acquisition Date** ____________ **Time** ________

Type of Source ____________________

Test Number ____________________ **Sample ID Number** ____________________

Sample Description ____________________

Analyst Responsible ________________ **Date Analyzed** ______________ **Time** __________

Calculations and Report Reviewed By ____________________ **Report Date** ____________

Workup

1. **Column Flow Rate (mL/min)** ____________ 2. **Recorder Speed** ____________

3. **Full Scale (mV)** ____________ 4. **Column Pressure (psi)** ____________

5. **Electrometer Set (A/mV)** ____________ 6. **Calibration Date** ____________

7. **Sample Size (mL)** ____________ 8. **Oven Temperature (°C)** ____________

9. **Flame Flow Rates (mL/min):** H_2 ____________ **Air** ____________

10. **Attenuation** ____________ 11. **Range** ____________

12. **Observations** ____________________

Results: **PPM value (in original sample) or I – interference; NC – not computed; NG – sample value below blank; ND – not detectable (< 2 σ blank or baseline).**

Gas	Uncorrected Sum of Peak Areas	Blank Valve	Retention Time	Corrected Sum of Peak Areas	Conc. (%)	Sensitivity	High/Low Calibration Standards	Conc. (ppm)
GC$_1$								
GC$_2$								
GC$_3$								
GC$_4$								
GC$_5$								
GC$_6$								
GC$_7$								

NO_x FIELD DATA

Sample Site ______________________________

____

Type of Source ______________________________

Sampling Location ______________________________

Sample Number ______________ **Date Taken** ______________ **Time** ______________

Temperature ______________ **Barometric** ______________ **Static Pressure** ______________

Analyst Responsible ______________ **Date Analyzed** ______________ **Time** ______________

Calculations and Report Reviewed By ______________ **Report Date** ______________

- -

Sampling Flask Number ______________________________

V_f (volume of flask plus valve, mL) ______________________________

v_a (volume of acidic, oxidizing solution) ______________________________

T_i (initial flask temperature, °K) ______________________________

$P_{b,i}$ (barometric pressure prior to sampling) ______________________________

$\Delta P_{m,i}$ (manometer reading prior to sampling) ______________________________

P_i (absolute internal flask pressure prior to sampling) = $P_{b,i} - \Delta P_{m,i}$ = ______________________________

T_f (flask temperature at sample recovery, °K) ______________________________

$P_{b,f}$ (barometric pressure at sample recovery) ______________________________

$\Delta P_{m,f}$ (manometer reading at sample recovery) ______________________________

P_f (absolute internal flask pressure at sample recovery) = $P_{b,f} - \Delta P_{m,f}$ = ______________________________

INORGANIC GASES ANALYSIS SHEET

Contractor ______________________________

Sample Site ______________ **Sample Acquisition Date** __________ **Time** __________

Type of Source ______________________________

Test Number ______________ **Sample ID Number** ______________

Sample Description ______________________________

Obtained By Grab: ____ **Yes** ____ **No** **Time Integrated From:** __________ **To** __________

Original Sample Volume or Mass ______________________________

Analyst Responsible ______________ **Date Analyzed** __________ **Time** __________

Calculations and Report Reviewed By ______________ **Report Date** __________

Type of Sampling Container ______________________________

Sampling Container Purged or Cleaned Prior to Sampling ______________________________

SULFUR SPECIES

1. Column Flow Rate (mL/min) ____________ 2. Recorder Speed ____________

3. Full Scale (mV) ____________ 4. Column Pressure (psi) ____________

5. Electrometer Set (A/mV) ____________ 6. Calibration Date ____________

7. Sample Size (mL) ____________ 8. Oven Temperature (°C) ____________

9. Attenuation ____________ 10. Range ____________

11. Observations ____________

12. Specify type of sampling container ____________

13. Are sample responses bracketed with standards? ____________

14. Analyst Responsible ____________ Date Analyzed ____________ Time ____________

15. Calculations and Report Reviewed By ____________ Report Date ____________

Gas	Uncorrected Sum of Peak Areas	Blank Value	Retention Time	Corrected Sum of Peak Areas	Conc. (%)	Sensitivity	High/Low Calibration Standards	Conc. (ppm)
COS								
H_2S								
SO_2								
CS_2								

Results: PPM value (in original sample) or I - interference; NC - not computed; NG - sample value below blank;
ND - not detectable (<2 σ blank or baseline).

FIXED GASES

1. Column Flow Rate (mL/min) ____________________ 2. Recorder Speed ____________________

3. Full Scale (mV) ____________________ 4. Column Pressure (psi) ____________________

5. Electrometer Set (A/mV) ____________________ 6. Calibration Date ____________________

7. Sample Size (mL) ____________________ 8. Oven Temperature (°C) ____________________

9. Attenuation ____________________ 10. Range ____________________

11. Observations ____

12. Analyst Responsible ____________________ Date Analyzed ____________________ Time ____________

13. Calculations and Report Reviewed By ____________________ Report Date ____________________

Gas	Uncorrected Sum of Peak Areas	Blank Value	Retention Time	Corrected Sum of Peak Areas	Conc. (%)	Sensitivity	High/Low Calibration Standards	Conc. (ppm)
O_2								
CO_2								
CO								
N_2								

Results: PPM value (in original sample) or I - interference; NC - not computed; NG - sample value below blank;
ND - not detectable (<2 σ blank or baseline).

NO_x ANALYSIS REPORT FORM

Sample # ____________________ **Date analyzed** ____________ **Time** ____________

Comments ____________________ **Analyst Responsible** ____________________

____________________ **Calculations and report checked by** ____________________

____________________ **Report Date** ____________________

1.1 Standardization

1.1.1 pH of standard solutions ____________________

1.1.2 A_1 (absorbance of the 100 μg NO_2 standard) ____________________

A_2 (absorbance of the 200 μg NO_2 standard) ____________________

A_3 (absorbance of the 300 μg NO_2 standard) ____________________

A_4 (absorbance of the 400 μg NO_2 standard) ____________________

1.1.3 K_c (calibration factor)

$$= 100 \left[\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \right]$$

$$= 100 \left[\frac{(\quad) + 2(\quad) + 3(\quad) + 4(\quad)}{(\quad)^2 + (\quad)^2 + (\quad)^2 + (\quad)^2} \right]$$

K_c =

1.2 Test Solution Analysis

1.2.1 V_f (volume of flask plus valve, mL) ____________________

V_a (volume of acidic, oxidizing solution) ____________________

T_i (initial flask temperature, °K) ____________________

$P_{b,i}$ (barometric pressure prior to sampling) ____________________

$\Delta P_{m,i}$ (manometer reading prior to sampling) ____________________

P_i (absolute internal flask pressure prior to sampling) $= P_{b,i} - \Delta P_{m,i} =$ ____________________

1.2.2 T_f (flask temperature at sample recovery, °K) ____________________

$P_{b,f}$ (barometric pressure at sample recovery) ____________________

$\Delta P_{m,f}$ (manometer reading at sample recovery) ____________________

P_f (absolute internal flask pressure at sample recovery) = $P_{b,f} - \Delta P_{m,f}$ = ____________________

1.2.3 V_{sc} (sample volume, dry basis, standard conditions, mL)

$$= \left(0.3858 \, \frac{°K}{\text{mm Hg}}\right) \left(V_f - V_a\right) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$

$$= \left(0.3858 \, \frac{°K}{\text{mm Hg}}\right) \left(\underline{(\quad)} - \underline{(\quad)}\right) \left[\frac{(\quad)}{(\quad)} - \frac{(\quad)}{(\quad)}\right]$$

V_{sc} =

1.2.4 Final test solution pH ____________________

A (test solution absorbance) ____________________

F (dilution factor, as needed to reduce the absorbance into the range of calibration ____________________

m (total µg NO_2 per sample)

$= 2 \, K_c \, AF$

$= (2) \; (\quad) \; (\quad) \; (\quad)$

m =

1.2.5 C (sample concentration, dry basis, standard conditions, mg/m^3)

$$= \left(10^3 \, \frac{\text{mg/m}^3}{\mu\text{g/mL}}\right) \frac{m}{V_{sc}}$$

$$= \left(10^3 \, \frac{\text{mg/m}^3}{\mu\text{g/mL}}\right) \frac{(\quad)}{(\quad)}$$

C =

FUGITIVE EMISSIONS FIELD DATA
GENERAL

Sample Site ____

____

Type of Source ____

Sampling Location ____

Test Number ______________________ **Sample Number** ______________________

Date Taken ______________________

Type of Sample: **Air** __________ **Water** __________

Sample Description ____

____

Analyst Responsible ______________ **Date Analyzed** ______________ **Time** ______________

Calculations and Report Reviewed By: ______________________ **Report Date** ______________

- -

SAMPLING DATA – AIR SAMPLE

Sampling Device ____

Size of High Volume Sample Filter ____

ANALYTICAL DATA – AIR SAMPLE

Sample Number	Sample Mass on Particulate Filter
	Gross ______________ Tare ______________ Net ______________
	Gross ______________ Tare ______________ Net ______________
	Gross ______________ Tare ______________ Net ______________
	Gross ______________ Tare ______________ Net ______________

Flow Rate ______________________ Sampling Time ______________________

Type and Size of Adsorbent Bed ______________________________________

____

Sample Location: Upwind ________ Downwind ________

Wind Speed ______________________ Wind Direction ______________________

Ambient Temperature ____

Distance From Source ____

- -

SAMPLING DATA – WATER SAMPLE

Sampling Device ____

Sample Volume ____

Composite Sample: Yes ________ No ________

If Composite, Number and/or Volumes of Portions of Composite ______________ / ______________

Sample Description: Fluid ________ Viscous ________ Hot ________ Cold ________ Flowing ________

Still ________ Homogeneous ________ Heterogeneous ________ Color ________

LIQUIDS FIELD DATA
GENERAL

Sample Site ____

____

Type of Source ____

Sampling Location ____

Sample Type: Aqueous ________ Slurry ________ Organic ________

Sample Number ______________________ **Date Taken** ______________________

Analyst Responsible ____

Calculations and Report Reviewed By ______________________ **Report Date** ____________

- -

Sampling Device ______________________ **Sample Mass or Volume** ______________________

Composite Sample: Yes ________ or No ________ .

If Composite, Number and/or Volume of Portions of Composite: ______________ / ______________

Sample Description: Fluid _____ Viscous _____ Hot _____ Cold _____ Flowing _____ Still _____

Homogeneous _____ Heterogeneous _____ Color _____

Sampling Problems ____

____

FIELD WATER ANALYSIS

Contractor ______________________________

Sample Site ____________________ **Sample Acquisition Date** ____________________

Type of Source ______________________________

Test Number ____________________ **Sample ID Number** ____________________

Sample Description ______________________________

Analyst Responsible ____________________ **Date Analyzed** ____________________ **Time** ____________

Calculations and Report Reviewed By ____________________ **Report Date** ____________________

Parameter	Uncorrected Sample Value	Blank Value	Corrected Sample Value	Sensitivity	High/Low Calibration Standards or Concentration Added	Assigned Concentration
Flow						m^3/h
pH						
Cond						µmhos/cm
TSS						mg/L
Hard						mg/L
Alk						mg/L
Acidity						mg/L
NH_3-N						mg/L
NO_3^--N						mg/L
Cyanide						mg/L
PO_4-P						mg/L
SO_3						mg/L
SO_4						mg/L

Results: Concentration measured in original sample on I - interference; NC - not computed; NG - sample value below blank; ND - not detectable ($<\sigma$ blank or baseline).

SOLIDS FIELD DATA
GENERAL

Sample Site ____

____

Type of Source ____

Sampling Location ____

Sample Type: **Inorganic** ____________________ **Organic** ____________________

Sample Number ____________________ **Date Taken** ____________________

Analyst Responsible ____

Calculations and Report Reviewed by: ____________________ **Report Date** ____________________

- -

Sampling Device ____________________ **Sample Mass or Volume** ____________________

Composite Sample: **Yes** __________ **or No** __________ .

If Composite, Number and/or Volume of Portions of Composite: ____________ / ____________

Sample Description: **Homogeneous** ______ **Heterogeneous** ______ **Powder** ______ **Small** ______ **Pieces** ______

Large Pieces ______ **Color** ______ **Wet** ______ **Dry** ______

Sampling Problems ____

____

SASS FIELD DATA

Plant ____________________
Date ____________________
Sampling Location ____________________
Source I.D. ____________________
Run Number ____________________
Operator ____________________
Ambient Temperature ____________________
Barometric Pressure ____________________
Static Pressure, (P_S) ____________________
Filter Number(s) ____________________
____

Probe Length and Type ____________________
Nozzle, I.D. ____________________
Assumed Moisture, % ____________________
XAD-2 Module Number ____________________
Meter Box Number ____________ Oven Number ____________
Meter ΔH. ____________________
C Factor ____________________
Probe Heater Setting ____________________
Oven Setting ____________________
Reference ΔP ____________________
Calculations and Report Checked By ____________ Report Date ______

SCHEMATIC OF TRAVERSE POINT LAYOUT
READ AND RECORD ALL DATA EVERY ___ MINUTES

TRAVERSE POINT NUMBER	SAMPLING TIME, MIN	CLOCK TIME (24 HR CLOCK)	GAS METER READING (V_M), FT^3	VELOCITY HEAD (ΔP_S) IN. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), IN H_2O		STACK TEMPERATURE (T_S), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM IN H_g	OVEN TEMPERATURE °F	IMPINGER TEMPERATURE °F	SORBENT TRAP TEMPERATURE °F	PROBE TEMPERATURE °F
					DESIRED	ACTUAL		INLET ($T_{M_{IN}}$) °F	OUTLET ($T_{M_{OUT}}$) °F					
TOTAL		●		●	●	●	●	●	●	●	●	●	●	●
AVERAGE	●	●	●	●	●					●	●	●	●	●

COMMENTS

EXAMPLE OF AN ACCEPTABLE SYSTEM OF SAMPLE CODING WITH COMMENTS FOR SAMPLE PACKING SHEETS

1C	**1-3μ cyclone catch**
3C	**3-10μ cyclone catch**
10C	**> 10μ cyclone catch**
PF-a	**Particulate filter(s)**
PR	**CH_2Cl_2/Methanol probe and cyclone rinse**
MR	**CH_2Cl_2 organic module rinse**
XR	**XAD-2 resin**
XRB	**XAD-2 resin blank**
CD-O	**Neat condensate**
CD-LE	**CH_2Cl_2 extract of condensate**
CD-AE	**Acidified, extracted condensate**
HM	**HNO_3 module rinse**
HMB	**HNO_3 blank**
HI	**First (H_2O_2) impinger - Special handling. See Chapter 2**
HIB	**First (H_2O_2) impinger blank - Special handling**
AI	**2nd and 3rd (APS) impinger composite**
AI-1B	**2nd (First APS) impinger blank**
AI-2B	**3rd (Second APS) impinger blank**
MCB	**CH_2Cl_2 blank**
MMB	**CH_2Cl_2/Methanol blank**
FF	**Liquid (oil) fuel feed**
CF	**Solid (coal) fuel feed**
FA	**Fly ash**
BA	**Bottom ash**

SAMPLE PACKING SHEET

Sample Site ______
Date Sampled ______
Shipped By ______
Date Shipped ______
Carrier ______

ID Number ______ **Test Number** ______
Invoice Number ______
Date Received ______
Received By ______
Condition ______

Sample No.	Collected (yes/no)	Date Recovered/Prep	Time	Weight (g) or Volume (mℓ)	Field Adjustments/Observations

Signature ______

Page 3 of ____

SAMPLE PACKING SHEET

Sample Site ________________
Date Sampled ________________
Shipped By ________________
Date Shipped ________________
Carrier ________________

ID Number __________ **Test Number** __________
Invoice Number ________________
Date Received ________________
Received By ________________
Condition ________________

Sample No.	Collected (yes/no)	Date Recovered/Prep	Time	Weight (g) or Volume (mℓ)	Field Adjustments/Observations
MR					
HM					
1C					
3C					
10C					
PR					
GC					
GF					
GP					
PF-a					

Page 2 of ____

SAMPLE PACKING SHEET

Sample Site __________
Date Sampled __________
Shipped By __________
Date Shipped __________
Carrier __________

ID Number __________ **Test Number** __________
Invoice Number __________
Date Received __________
Received By __________
Condition __________

Sample No.	Collected (yes/no)	Date Recovered/Prep	Time	Weight (g) or Volume (mℓ)	Field Adjustments/Observations
MCB					
MAB					
HMB					
HIB					
AI-1B					
AI-2B					
XRB					
CD-O					
CD-LE					
CD-AE					
HI					
AI					
XR					

Page 1 of ____

PARTICULATE LOADING DATA

Date Weighed T ______________________________

Date Weighed G ______________________________

Balance Used ______________________________

Analyst Responsible ______________________________

Date Analyzed ______________________________ Time ______________________________

Calculations and Report Reviewed By ______________________________ Report Date ______________________________

Give Gross (G), Tare (T), and Net (N) Weights and Units for All Applicable Samples

Sample No. and Site Name and Location	Particulate Filter	1μ Cyclone	3μ Cyclone	10μ Cyclone	Probe Rinse Solids
	G T N	G T N	G T N	G T N	G T N
	G T N	G T N	G T N	G T N	G T N
	G T N	G T N	G T N	G T N	G T N
	G T N	G T N	G T N	G T N	G T N
	G T N	G T N	G T N	G T N	G T N

SASS ANALYTICAL DATA

Plant ____________________ Sample No. __________

Sampling Location ____________________ Run No. __________

Recovered By __________ Recovery Date __________ Run Date __________

Comments ____________________

Analyst Responsible ____________________

Calculations and Report Reviewed By __________ Report Date __________

FILTERS USED

No. __________

____

____

____

____

CYCLONES

	Used (yes/no)	Pretared Container (No.)
10μ	__________	__________
3μ	__________	__________
1μ	__________	__________

IMPINGER VOLUMES

	Initial	Final
First (H_2O_2)	__________ mℓ	__________ mℓ
Second (APS + $AgNO_3$)	__________ mℓ	__________ mℓ
Third (APS + $AgNO_3$)	__________ mℓ	__________ mℓ
TOTALS	__________ mℓ	__________ mℓ

Gain __________ mℓ

SILICA GEL WEIGHTS

	Initial	Final
	__________ g	__________ g
	__________ g	__________ g
	__________ g	__________ g
TOTALS	__________ g	__________ g

Gain __________ g

CONDENSATE

TOTAL VOLUME COLLECTED __________ mℓ

Volume Neat __________ mℓ

Volume Extracted __________ mℓ

Volume $CH_2C\ell_2$ Extract (3 x _____ mℓ) __________ mℓ

Extracted Condensate: pH Neat __________

Amount 96% HNO_3 added __________

pH Final __________

TOTAL GAIN __________ mℓ

SSMS ANALYSIS SHEET

Contractor

Sample Site Sample Acquisition Date

Type of Source

Test Number Sample ID Number

Sample Description

Analyst Responsible Date Analyzed Time

Calculations and Report Reviewed By Report Date

Instrument Resolution

Sequential Exposure Factor Carbon Type Used for Electrode Preparation

Description of Multielement Calibration Standard

Internal Standard(s)

Original Sample Volume or Mass

Dilution Factor

Brief Description of Electrode Preparation

Time at start and finish	Photo-plate exposure	Exposure x 10^{9} coulombs	Range factors		Meter or counter	Pulse repetition rate c/s	Pulse length microsec	Spark volt %	Magnet current mA	Accelerating voltage kV	Anal. pressure "torr"	Source pressure "torr"	Remarks
			Int.	Mon.									
	1												
	2												
	3												
	4												
	5												
	6												
	7												
	8												
	9												
	10												
	11												
	12												
	13												
	14												
	15												

Operator:

Element	Line Used for Estimate (mass number)	Uncorrected Sample Value	Blank Value	Corrected Sample Value	Assigned Concentration*	At Source Mass/Volume mg/m^3 or μg/L	Detection Limit
Uranium							
Thorium							
Bismuth							
Lead							
Thallium							
Mercury							
Gold							
Platinum							
Iridium							
Osmium							
Rhenium							
Tungsten							
Tantalum							
Hafnium							
Lutecium							
Ytterbium							
Thulium							
Erbium							
Holmium							
Dysprosium							
Terbium							
Gadolinium							
Europium							
Samarium							
Neodymium							
Praseodymium							

*Results: μg/g (in original sample) or I - interference; NC - not computed; NG - sample value below blank; ND - not detectable ($<2\sigma$ blank or baseline).

Element	Line Used for Estimate (mass number)	Uncorrected Sample Value	Blank Value	Corrected Sample Value	Assigned Concentration*	At Source Mass/Volume mg/m^3 or μg/L	Detection Limit
Cerium							
Lanthanum							
Barium							
Cesium							
Iodine							
Tellurium							
Antimony							
Tin							
Indium							
Cadmium							
Silver							
Palladium							
Rhodium							
Ruthenium							
Molybdenum							
Niobium							
Zirconium							
Yttrium							
Strontium							
Rubidium							
Bromine							
Selenium							
Arsenic							
Germanium							
Gallium							
Zinc							

*Results: μg/g (in original sample) or I - interference; NC - not computed; NG - sample value below blank; ND - not detectable ($<2\sigma$ blank or baseline).

Element	Line Used for Estimate (mass number)	Uncorrected Sample Value	Blank Value	Corrected Sample Value	Assigned Concentration*	At Source Mass/Volume mg/m^3 or µg/L	Detection Limit
Copper							
Nickel							
Cobalt							
Iron							
Manganese							
Chromium							
Vanadium							
Titanium							
Scandium							
Calcium							
Potassium							
Chlorine							
Sulphur							
Phosphorus							
Silicon							
Aluminum							
Magnesium							
Sodium							
Fluorine							
Oxygen							
Nitrogen							
Carbon							
Boron							
Beryllium							
Lithium							
Hydrogen							

*Results: µg/g (in original sample) or I - interference; NC - not computed; NG - sample value below blank; ND - not detectable ($<2\sigma$ blank or baseline).

AAS ANALYSIS SHEET

Contractor ______________________________

Sample Site ____________________ **Sample Acquisition Date** ____________________

Type of Source ______________________________

Test Number ____________________ **Sample ID Number** ____________________

Sample Description ______________________________

Original Sample Volume or Mass ______________________________

Analyst Responsible ____________________ **Date Analyzed** ____________ **Time** ____________

Calculations and Report Reviewed By ____________________ **Report Date** ____________________

	As	Hg	Sb
Instrument Used			
Wavelength Setting (nm)			
Lamp Current (ma)			
Fuel/Oxidizer Pressures (psi)			
PM Voltage (volts)			
Detection Limit (μg)			
Sensitivity (abs. units/ppm/ sample volume)			
High/Low Calibration Standards (ppm)			
Sample Aliquot Volume (mL)			
Dilution Factor			
Uncorrected Sample Aliquot Value (ppm)			
Blank Value (ppm)			
Corrected Sample Aliquot Value (ppm)			
Assigned Concentration*			
At Source Mass/Volume, mg/m^3 or μg/L			

***Results:** **PPM value (in original sample) or I - interference; NC - not computed; NG - sample value below blank; ND - not detectable (<2σ blank or baseline).**

IC ANALYSIS SHEET

Contractor ______________________________

Sample Site ____________________ **Sample Acquisition Date** ____________________

Type of Source ______________________________

Test Number ____________________ **Sample ID Number** ____________________

Sample Description ______________________________

Analyst Responsible ______________ **Date Analyzed** ______________ **Time** ______________

Calculations and Report Reviewed By ____________________ **Report Date** ______________

Instrument ______________________________

Eluent ____________________

Column Flow Rate ______________ **Pressure** ______________ **Recorder Speed** ______________

Sample Size ____________________ **Attenuator Setting** ____________________

Original Sample Volume or Mass ______________ **Multiple Standard Addition: Yes** ________ **No** ________

Observations ______________________________

Ion	Uncorrected Sample Value	Blank Value	Corrected Sample Value	High/Low Calibration Standards or Concentration Added	Dilution Factor	Assigned Concentration*	Detection Limit*
F^-							
Cl^-							
Br^-							
NO_2^-							
NO_3^-							
$SO_3^=$							
$SO_4^=$							
$PO_4^{\equiv}$							

*Results: μg/L values (in original sample or I – Interference; MC – major constituent, not quantified; NC – not computed; NG – sample value below blank; ND – not detectable ($< 2\ \sigma$ blank or baseline).

LC ANALYSIS REPORT

Contractor ______________________________

Sample Site ____________________ **Sample Acquisition Date** ____________________

Type of Source ______________________________

Test Number ____________________ **Sample ID Number** ____________________

Sample Description ______________________________

Original Sample Volume or Mass ______________________________

Analyst Responsible ____________________ **Date Analyzed** ____________________ **Time** __________

Calculations and Report Reviewed By ____________________ **Report Date** ____________________

Column Flow Rate ____________________ **Column Temperature** ____________________

Observations ______________________________

	TCO mg	GRAV mg	TCO + GRAV Total mg	Concentration mg/ (m³, L, or kg)[5]
Total Sample[1]				
Taken for LC[2]				
Recovered[3]				

Fraction	TCO in mg				GRAV in mg				TCO + GRAV Total mg	Concentration mg/ (m³, L, or kg)[5]
	Found in Fraction	Blank	Cor-rected	Total[4]	Found in Fraction	Blank	Cor-rected	Total[4]		
1										
2										
3										
4										
5										
6										
7										
Sum										

1. Quantity in entire sample, determined before LC
2. Portion of whole sample used for LC, actual mg
3. Quantity recovered from LC column, actual mg
4. Total mg computed back to total sample
5. Supply values for both sample size and concentration

IR ANALYSIS REPORT

Contractor ____

Sample Site ____________________ Sample Acquisition Date ____________

Type of Source ____

Test Number ____________________ Sample ID Number ____________

Sample Description ____

Analyst Responsible ______________ Date Analyzed __________ Time __________

Calculations and Report Reviewed By ____________________ Report Date ____________

Instrument ____________________ Sample Cell Type ____________

Utilized Max/Min Signal Intensity Values ________________________________

Observations ____

____

IR REPORT

SAMPLE:____

Wave Number (cm^{-1})	**Intensity**	**Assignment** **Comments**

LRMS ANALYSIS REPORT

Contractor ______________________________

Sample Site ____________________ **Sample Acquisition Date** ____________________

Type of Source ______________________________

Test Number ____________________ **Sample ID Number** ____________________

Sample Description ______________________________

Analyst Responsible ____________________ **Date Analyzed** ____________ **Time** ____________

Calculations and Report Reviewed By ____________________ **Report Date** ____________

Instrument ______________________________

Resolution ______________________________

Sample Size ____________ **Batch Inlet** ____________ **Probe Inlet** ____________

Observations ______________________________

____

LRMS REPORT

SAMPLE: ____________________

Major Categories

Intensity	Category	MW Range

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition

Other

ORGANIC EXTRACT SUMMARY REPORT

Contractor ______________________________

Sample Site ______________ **Sample Acquisition Date** ______________

Type of Source ______________________________

Test Number ______________ **Sample ID Number** ______________

Sample Description ______________________________

Original Sample Volume or Mass ______________________________

Analyst Responsible ______________ **Date Analyzed** __________ **Time** __________

Calculations and Report Reviewed By ______________ **Report Date** __________

ORGANIC EXTRACT SUMMARY TABLE

Sample ______________________

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg								
TCO, mg								
GRAV, mg								

Category

Assigned intensity – mg/___ (m^3, L, or kg)[1]

---

[1] Concentration for gas samples = mg/m^3, for liquid samples = mg/L, for solid samples = mg/kg. Fill in actual m^3, L, or kg value.

ALGAL BIOASSAY DATA SHEET

Sample ID Number ____________________

Test Date ____________________

Date Sample Received ____________________

Culture Medium ____________________

Test Number ____________________

pH of Medium ____________________

Report Date ____________________

Temperature ____________________

Collection Data (Time-Date) ____________________

Illumination Source ____________________

Other Pertinent Sample Information ____________________

Intensity ____________________

Investigator ____________________

Duration ____________________

Calculations and Report Reviewed By ____________________

RESULTS

Sample Flask No.	Conc.	INCUBATION TIME-DAYS									
		3			5			7			
		Cells/mL	Dry wt. mg/L	Other	Cells/mL	Dry st. mg/L	Other	Cells/mL	Dry wt. mg/L	Other	(Etc. for 9, 13, 17, 21 Days)

REMARKS:

Maximum Specific Growth Rate:
Maximum Standing Crop:
EC 50 (12 Day or Other Days of Importance)

BIOASSAY RECORD SHEET

Dilution Water Analysis

Date	Hardness mg/L as CaCo$_3$	Alkalinity mg/L as CaCo$_3$	Specific Conductance	pH	Suspended Solids mg/L	TOC mg/L	Un-ionized Ammonia mg/L	Residual Chlorine mg/L	Total Organo Phos. Pesticides mg/L	Total Organo Chlor. Pesticides + PCB's mg/L

MICROSCOPIC PARTICLE CHARACTERIZATION

Contractor ____________________

Sample Site ____________________ Sample Acquisition Date ____________________

Type of Source ____________________

Test Number ____________________ Sample ID Number ____________________

Brief Sample Description ____________________

Microscopist ____________________ Date Analyzed ____________________

Calculations and Report Reviewed By ____________________ Report Date ____________________

Prepare a separate data sheet for each mounting or particle type.

Gross Sample Appearance ____________________

Particle Type ________________________________

Percent by Number ________________ **% Estimated** ____________

Materials Preparation ____________________________

Mounting Media ______________________________

Microscope Used: ____________ **Objective Lens** ________ **Ocular Lens** ________

Illumination: **Type** ________ **Source** ________ **Combined Magnification** ________

PHYSICAL PROPERTIES

Shape ________________________________

Size Range of This Particle Type ________________________

Aggregation: **Clustered** ________ , **Distinct** ________ , **Other** ________

Homogeneity: **Homogeneous** ________ , **Laminar** ________ , **Polycrystalline** ________

Heterogeneous ________________

Inclusions ________________

Surface Texture: **Glassy** ______ , **Smooth** ______ , **Porous** ______ , **Rough** ______

Other ________________________

Other Comments ______________________________

OPTICAL PROPERTIES

Transparent __________ , **Translucent** __________ , **Opaque** __________

Color Observed from Transmitted Light ____________________

Color Observed of Reflected Light ____________________

Luster: **Metallic** ____ , **Adamantine** ____ , **Vitreous** ____ , **Resinous** ____ , **Greasy** ____ , **Silky** ____

Brilliance: **Splendent** ____ , **Shining** ____ , **Glistening** ____ , **Glimmering** ____ , **Dull** ____

Isotropic ____ , **Anisotropic** ____

Refractive Index Estimate ____________ **Birefringence Estimate** ____________

Other ________________________________

____

Photographs Attached ________ **or Negative #** ________ **Scale Indication** ________

WI-38 CELLULAR TOXICITY TESTING

Sample ID Number ____________________

Date Sample Received ____________________

Description of Sample ____________________

____

Date Tested ____________________

Report Date ____________________

Passage of Cells ____________________

Seeding Population of Cells ____________________

Incubation Time ____________________

Incubation Temperature ____________________

EC_{50} VALUES

Cell Count ____________________

Viability ____________________

Viability Index ____________________

Protein ____________________

ATP ____________________

Other ____________________

Investigator ____________________

Calculations and Report Reviewed By ____________________

TEST RESULTS

Tube No.	Test Sample Conc. μg/mL) or(μL/mL)	pH		Cell No. as % of Control	Viable Cells	Viability Index	ATP	Protein
		Initial	After Incub.					

ALVEOLAR MACROPHAGE TOXICITY TESTING

Sample ID Number ____________________
Date Sample Received ____________________
Description of Sample ____________________
____
Date Tested ____________________
Report Date ____________________
No. Rabbits Used ____________________
Remarks About Rabbits ____________________
____
Total No. Cells Recovered ____________________
Seeding Population of Cells ____________________
Incubation Temperature ____________________

DIFFERENTIAL ____________________
Macrophages ____________________
Neutrophils ____________________
Other ____________________
Incubation Time ____________________
EC_{50} Values ____________________
Cell Count ____________________
Viability ____________________
Viability Index ____________________
Protein ____________________
Other ____________________
Investigator ____________________

Calculations and Report Reviewed By ____

TEST RESULTS

Tube No.	Test Sample Conc. µg/mL) or(µL/mL)	pH		Cell No. as % of Control	Viable Cells	Viability Index	ATP	Protein
		Initial	After Incub.					

GENERAL FORMAT FOR RECORDING MUTAGENICITY DATA

Date Sample Received ____________________

Sample ID Number ____________________

Incubation Temperature ____________________

Incubation Start __________ __________

Incubation End ____________________

Investigator ____________________

Tester Strain Used ____________________

Report Date ____________________

Date Tested ____________________

Date Repeated ____________________

Comments, i.e., Solvent Extraction or Sample Pretreatment etc.

____

Calculations and Report Reviewed By ____________________

Test Condition	Sample Type	Assay Amount (µg/plate)	Revertants or colonies on Individual Plates				Average		Adjusted Average Revertants		Index of Relative Mutagenicity	
			Number 1	Number 2	Repeat 3	Repeat 4	1&2	3&4	1&2	3&4	1&2	3&4
Nonactivation	Positive control											
	Solvent control											
	Sample Plate ID											
	Toxicity test											
Induced activation	Positive control											
	Solvent control											
	Sample Plate ID											
	Toxicity test											

STATIC BIOASSAY RECORD SHEET

Sample ID Number **Source** **Date Sample Received**
Investigator
Test Number **Date/Time Initiated**
Source of Dilution Water **Date/Time Completed**
Test Species **Temperature Range**
Number Individuals Per Percent Waste
Calculations and Report Reviewed By **Report Date**

	Start									Comments
Percent waste									Control	
DO										
Temperature										
pH										
Specific conductance										*
	24 hours									LC_{50}/EC_{50}
Number surviving										
% survival										
DO										
Temperature										
pH										
	48 hours									
Number surviving										
% survival										
DO										
Temperature										
pH										
	96 hours									
Number surviving										
% Survival										
DO										
Temperature										
pH										

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* Method used for calculating.

APPENDIX B

PREPARATION OF XAD-2 SORBENT RESIN

APPENDIX B

PREPARATION OF XAD-2 SORBENT RESIN

B.1 SCOPE AND APPLICATION

XAD-2 resin, as supplied by the manufacturer, is impregnated with a bicarbonate solution to inhibit microbial growth during storage. Both the salt solution and any residual extractable monomer and polymer species must be removed before use. The resin is prepared by a series of water and organic extractions followed by careful drying.

B.2 EXTRACTION

B.2.1 Method 1

The procedure may be carried out in a giant Soxhlet extractor, which will contain enough XAD-2 for a single SASS module. An all-glass thimble (55-90 mm OD x 250 mm deep [top to frit]) containing an extra-coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenulated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and stainless steel screen since it floats on the final solvent, methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse with 1 L H_2O for 1 cycle, then discard H_2O
Water	Extract with H_2O for 8 hours
Methyl alcohol	Extract for 22 hours
Methylene chloride	Extract for 22 hours
Methylene chloride (fresh)	Extract for 22 hours

B.2.2 Method 2

As an alternate to Soxhlet extraction, a continuous extractor has also been fabricated for the extraction sequence and is described in Figure B-1. This extractor has been found to be acceptable. The particular canister used for the apparatus shown in Figure B-1 contains about 500 g of finished XAD-2 or enough for more than three sorbent modules. Any size may be constructed; the choice is dependent on the needs of the sampling programs. The XAD-2 is held under light spring tension between a pair of coarse and fine screens. Spacers under the bottom screen allow for even distribution of clean solvent. The three-necked flask should be of sufficient size (3 L in this case) to hold solvent equal to twice the dead volume of the XAD-2 canister. Solvent is refluxed through the Snyder column and the distillate continuously cycled up through the XAD-2 for extraction and returned to the flask. The flow is maintained upwards through the XAD-2 to allow maximum solvent contact and prevent channeling. A valve at the bottom of the canister allows removal of solvent from the canister between changes.

Experience has shown that it is very difficult to cycle sufficient water in this mode. Therefore, the aqueous rinse is accomplished by simply flushing the canister with about 20 L of distilled water. A small pump may be useful for pumping the water through the canister. The water extraction should be carried out at the rate of about 20-40 mL/min.

After draining the water, subsequent methyl alcohol and methylene chloride extractions are carried out using the refluxing apparatus. An overnight or 10- to 20-hour period is normally sufficient for each extraction.

All materials of construction are glass, Teflon, or stainless steel. Pumps, if used, should not contain extractable materials. Pumps are not used with methanol and methylene chloride.

B.3 DRYING

After evaluation of several methods of removing residual solvent, a fluidized-bed technique has proven to be the fastest and most reliable drying method.

A simple column with suitable retainers as shown in Figure B-2 will serve as a satisfactory column. A 10.2-cm (4-in.) Pyrex pipe 0.6 m (2 ft)

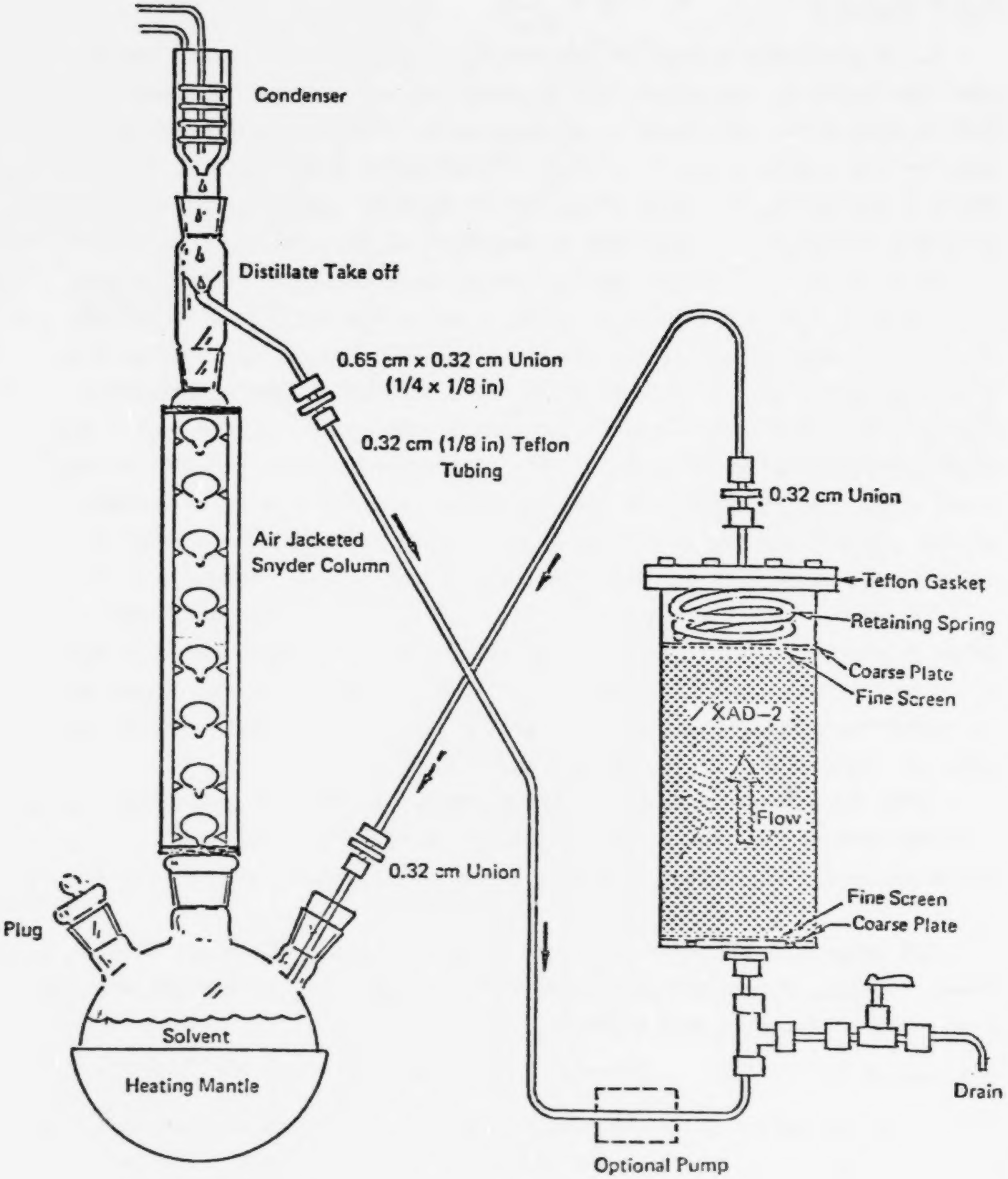
Condenser
Distillate Take off
0.65 cm x 0.32 cm Union
(1/4 x 1/8 in)
0.32 cm (1/8 in) Teflon
Tubing
0.32 cm Union
Air Jacketed
Snyder Column
Teflon Gasket
Retaining Spring
Coarse Plate
Fine Screen
XAD–2
Flow
0.32 cm Union
Fine Screen
Coarse Plate
Plug
Solvent
Heating Mantle
Drain
Optional Pump

Figure B-1. XAD-2 cleanup extraction apparatus.

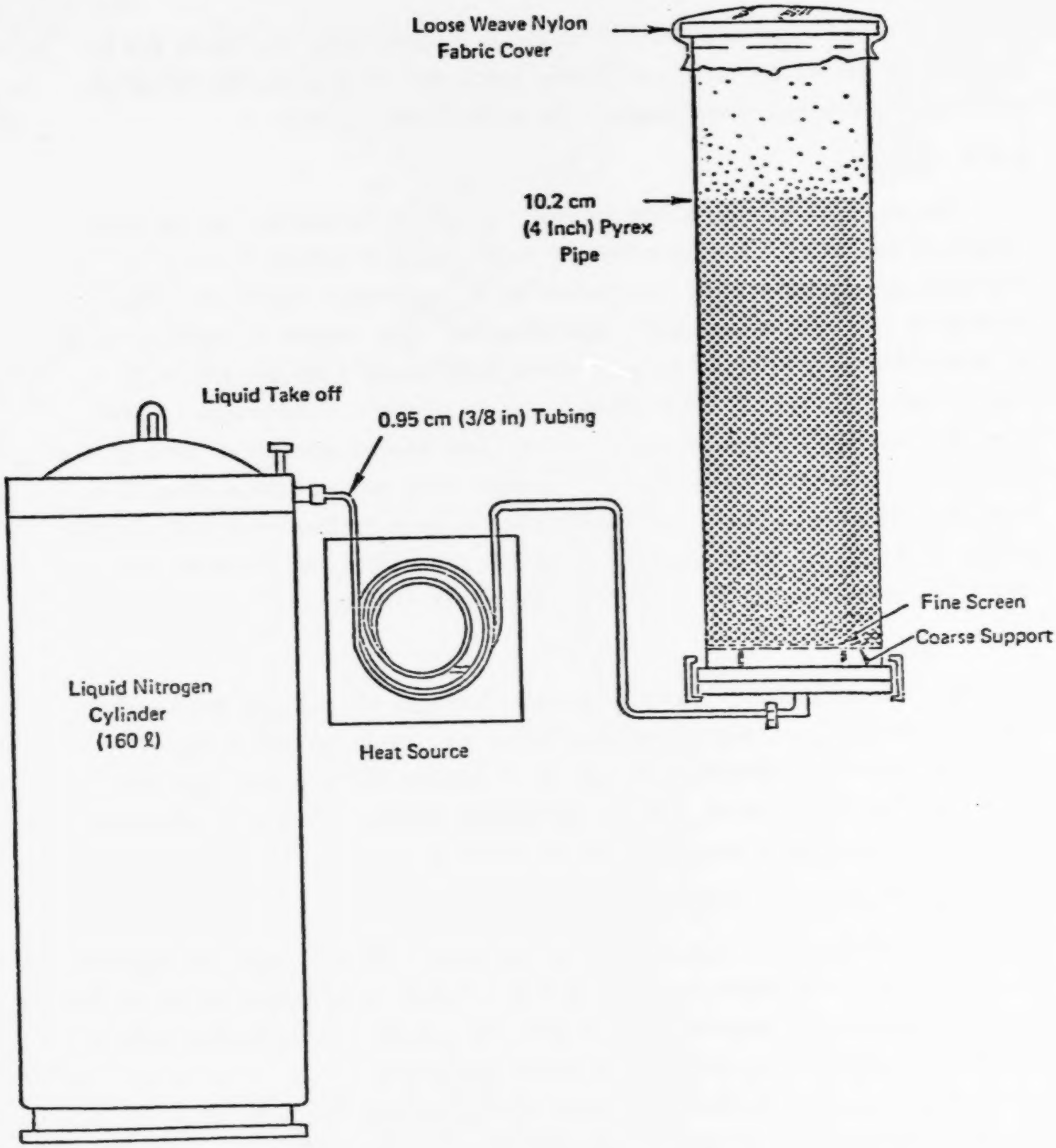
Loose Weave Nylon
Fabric Cover
10.2 cm
(4 Inch) Pyrex
Pipe
Liquid Take off
0.95 cm (3/8 in) Tubing
Fine Screen
Coarse Support
Liquid Nitrogen
Cylinder
(160 ℓ)
Heat Source

Figure B-2. XAD-2 fluidized-bed drying apparatus.

long will hold all of the XAD-2 from the extractor shown in Figure B-1 or the Soxhlet extractor, with sufficient space for fluidizing the bed while generating a minimum resin load at the exit of the column.

B.3.1 Method 1

The gas used to remove the solvent is the key to preserving the cleanliness of the XAD-2. Liquid nitrogen from a regular commercial liquid nitrogen cylinder has routinely proven to be a reliable source of large volumes of gas free from organic contaminants. The liquid nitrogen cylinder is connected to the column by a length of precleaned 0.95-cm (3/8-in.) copper tubing, coiled to pass through a heat source. As nitrogen is bled from the cylinder, it is vaporized in the heat source and passes through the column. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40° C. Experience has shown that about 500 g of XAD-2 may be dried overnight consuming a full 160-L cylinder of liquid nitrogen.

B.3.2 Method 2

As a second choice, high purity tank nitrogen may be used to dry the XAD-2. The high purity nitrogen must first be passed through a bed of activated charcoal approximately 150 mL in volume. With either type of drying method, the rate of flow should gently agitate the bed. Excessive fluidization may cause the particles to break up.

B.4 QUALITY CONTROL PROCEDURES

For both Methods 1 and 2, the quality control results must be reported for the batch. The batch must be reextracted with methylene chloride if the residual extractable organics are greater than 20 μg/mL or the gravimetric residue is greater than 0.5 mg/20 g XAD-2 extracted.

Three control procedures are used with the final XAD-2 to check for (1) residual methylene chloride, (2) extractable organics (TCO), and (3) residue (GRAV).

B.4.1 Procedure for Residual Methylene Chloride

B.4.1.1 Description--

A 1 ±0.1 g sample of dried resin is weighed into a small vial, 3 mL of toluene are added, and the vial is capped and well shaken. Five microliters of toluene (now containing extracted methylene chloride) are injected into a gas chromatograph, and the resulting integrated area is compared to a reference standard.

The reference solution consists of 2.5 μL of methylene chloride in 100 mL of toluene, simulating 100 μg residual methylene chloride on the resin. The acceptable maximum content is 1,000 μg/g resin.

B.4.1.2 Experimental--

- 6 ft. x 1/8 in. SS column containing 10% OV-101 on 100/120 Supelcoport
- Helium carrier at 30 mL/min
- FID operated on 4×10^{-11} A/mV
- Injection port temp 250° C, detector temp 305° C
- Programmed: 30° C (4 min) $\underline{40°/\text{min}}$ 250° C (hold)
  Program terminated at 1000 seconds.

B.4.2 Procedure for Residual Extractable Organics

B.4.2.1 Description--

A 20 ±0.1 g sample of cleaned, dried resin is weighed into a precleaned alundum or cellulose thimble which is plugged with cleaned, glass wool. (Note that 20 g of resin will fill a thimble, and the resin will float out unless well plugged.) The thimble containing the resin is extracted for 24 h with 200 mL of pesticide-grade methylene chloride.*

The 200-mL extract is reduced in volume to 10 mL using a nitrogen evaporation stream. Five microliters of that solution are analyzed by gas chromatography using the TCO analysis procedure. The concentrated solution should not contain more than 20 μg/mL of TCO extracted from the XAD-2. This is equivalent to 10 μg/g of TCO in the XAD-2 and would correspond to 1.3 mg of TCO in the extract of the 130-g XAD-2 module. Care should be taken to correct the TCO data for a solvent blank prepared (200 → 10 mL concentration) in a similar manner.

B.4.2.2 Experimental--

Use the TCO analysis conditions described in the revised Level 1 manual.

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*Burdick & Jackson pesticide grade or equivalent purity.

B.4.3 Methodology for Residual Gravimetric Determination.

After the TCO value is obtained for the resin batch by the above procedures, dry the remainder of the extract in a tared vessel. There must be less than 0.5 mg residue registered or the batch of resin will have to be extracted with fresh methylene chloride again until it meets this criteria. This level corresponds to 25 μg/g in the XAD-2 or about 3.25 mg in a resin charge of 130 g.

APPENDIX C

PARR BOMB COMBUSTION PROCEDURE

APPENDIX C

PARR BOMB COMBUSTION PROCEDURE

C.1 SCOPE AND APPLICATION

Parr oxygen combustion is applicable for the preparation of all combustible materials for inorganic analysis. For Level 1 samples, samples principally organic in nature are to be combusted, for example, fuel oil, coal, and XAD-2 resin. Significant background quantities of Cr, Fe, Ni, and Mn can be encountered as a result of attack on and leaching of stainless steel bomb components during combustion. To eliminate this background, samples for SSMS analysis are combusted by a more rigorous method using platinum electrodes and a quartz cup and lid to line the bomb.

C.2 APPARATUS

- Parr oxygen bomb--342-mL capacity
- Quartz cup and lid as bomb liner
- Platinum firing wire
- Oxygen supply and regulator
- Parr pellet press and die
- Vycor sample cups
- Glass beakers, 250 mL and 100 mL
- Watch glasses
- Whatman filters, #41
- Nalgene funnels
- Mortar and pestle, ceramic

C.3 REAGENTS

- 4 percent collodion in amyl acetate or equivalent.
- 1:1 HNO_3, H_2O
- Benzoic acid

C.4 SAMPLE PREPARATION

Two general types of sample will be analyzed: organic liquids and organic solids. A special sample type is the XAD-2 resin. No special preparation is necessary for the organic liquids; however, the other two sample types will require the following steps to insure complete combustion.

C.4.1 Organic Solids

Weigh 1.0 g solid or a quantity having a heat of combustion <8.0 Kcal, whichever is less, into a Vycor sample cup; add 0.25 g of benzoic acid and mix. Transfer contents to a pellet die and press the sample into a pellet.

C.4.2 XAD-2 Resin

Weigh 1.0 g of resin into a Vycor sample cup. Add ~1 mL of collodion solution, mix, and flatten the sample into a pellet. Place the sample in an oven at 110° C for ~20 min.

C.5 COMBUSTION PROCEDURE

C.5.1 SSMS Analysis Samples

Place 1 mL of 1:1 HNO_3 in a quartz cup and place in a Parr bomb. Place the Vycor cup with sample in a Pt holder and attach the platinum firing wire, being certain contact is made with the sample. The quartz cup and lid should fit the bomb snugly. Care must be taken when placing the quartz lid down onto the cup to assure that the lid forms a seal with the cup. Assemble the bomb and pressurize to 30 atm with O_2. Insert the bomb in a calorimeter, attach electrical leads, and ignite. Allow to cool for ~15 minutes and slowly release the pressure. Disassemble bomb and wash the bottom of the quartz lid and the contents of the Vycor sample cup into the quartz cup. Remove the quartz cup, wash the contents into a Nalgene bottle, and make up to 50 mL. Label the sample.

C.5.2 Other Samples (not sensitive to Parr bomb contamination)

Place 1 mL of 1:1 HNO_3 in the bottom of the Parr bomb. Place the sample cup in the holder and attach the platinum firing wire, being certain contact is made with the sample. Assemble the bomb and pressurize to 30 atm with O_2. Insert the bomb in a calorimeter, attach electrical leads, and ignite. Allow to cool for ~15 minutes and slowly relieve pressure. Disassemble bomb and wash contents into 250-mL beaker, cover with a watch glass, and digest on a hot plate for 30 min; do not allow to boil. Cool and filter through a #41 Whatman filter, supported in a Nalgene funnel, into a 100-mL Nalgene volumetric. Dilute to volume and label.

APPENDIX D

AQUA REGIA DIGESTION PROCEDURE

APPENDIX D

AQUA REGIA DIGESTION PROCEDURE

D.1 SCOPE AND APPLICATION

Aqua regia digestion is applicable for the preparation of loose particulate, particulate collected on glass fiber filters, and bulk solids (e.g., fly ash and bottom ash) for inorganic analysis. This method is appropriate for elements such as Hg, and anions such as $SO_4^{=}$, $PO_4^{\equiv}$, and F^-, which are soluble in aqua regia.

D.2 APPARATUS

- Distillation flasks, flat-bottom, 200 mL
- Condenser, Liebig or Allihn type
- Hot plate
- Volumetrics, Nalgene, 100 mL
- Filter funnels, Nalgene
- Filter paper, Whatman #41

D.3 REAGENTS

- Constant boiling aqua regia--4 parts concentrate HNO_3 + 1 part concentrate HCl; mix fresh daily

D.4 PROCEDURE

The weighed sample aliquot is placed in the distillation flask. Sixty milliliters of constant boiling aqua regia solution are added, the condenser is attached, and the apparatus is secured over a hot plate. The acid is refluxed for ~6 hours at which time the apparatus is removed from the hot plate and allowed to cool. Rinse the contents of the condenser into the distillation flask using 10 mL of deionized water and disconnect the condenser. Filter the contents of the distillation flask through a #41 Whatman filter supported by a Nalgene funnel. Collect the filtrate in a Nalgene volumetric and wash the filter with two 10-mL volumes of deionized water. Fill the volumetric to volume and label.

APPENDIX E

PROCEDURE FOR LEACHING OF BULK SOLIDS

APPENDIX E

PROCEDURE FOR LEACHING OF BULK SOLIDS*

E.1 SCOPE AND APPLICATION

The procedure described here is to be used to leach, or extract, trace, minor, and major soluble species from bulk solids. The procedure is intended as a means of obtaining solutions for the estimation of the relative environmental hazard inherent in the leachings of these bulk solids.

E.2 SUMMARY OF METHOD

A known weight of solid is shaken with deionized and distilled water. The aqueous phase is then separated by filtration and analyzed using SSMS and AAS.

E.3 APPARATUS

- Agitation equipment - Agitation equipment of any type that will produce constant movement of the aqueous phase equivalent to that of a reciprocating platform shaker operated at 60 to 70 one-inch (25-mm) strokes per minute without incorporation of air is suitable. Equipment used shall be designed for continuous operation without heating the samples being agitated.

- Membrane filter assembly - A borosilicate glass or stainless steel funnel with a flat, fritted base of the same material and membrane filters.

- Containers - Round, wide-mouth bottles of composition suitable to the nature of the waste and the analyses to be performed. One-gallon (or 4-L) bottles should be used with 700-g samples and ½-gal (or 2-L) bottles with 350-g samples. Multiples of these sizes may be used for larger samples. These sizes were selected to establish suitable geometry and provide that the sample plus liquid would occupy approximately 80 to 90 percent of the container. Bottles must have a watertight closure. Containers for samples where gases may be released should be provided with a venting mechanism. Containers should be cleaned in a manner consistent with the analyses to be performed.

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*Proposed Method for Leaching of Waste Materials, ASTM, 1916 Race St., Philadelphia, Pennsylvania 19103.

E.4 REAGENTS

- Test water--reagent grade; deionized plus distilled.

E.5 PROCEDURE

1. Grind the material, if necessary, to pass through a 9.5-mm (3/8-in.) standard sieve.
2. Dry the sample 18 ±2 h at 104 ±2° C. Cool to room temperature in a dessicator.
3. Weigh a representative 700- or 350-g portion of the material to be tested. Record the value to ±0.1 g.
4. Place the weighed portion of sample into the container to be used in the shake test.
5. Add to the container a volume of test water equal in milliliters to four times the weight in grams of the sample used in 4.
6. Close the container and place it on the agitation equipment.
7. Agitate continuously for 48 h ±0.5 h at 20 ±2° C.
8. Open the containers. Observe and record any changes in the sample and leaching solution.
9. Separate the bulk of the aqueous phase from any solid or nonaqueous phases by decantation, centrifugation, or filtration through filter paper, as appropriate. Vacuum filter the aqueous phase through a 0.45-μm membrane filter.
10. Transfer the filtrate to sample bottles of a size such that the entire bottle is filled. Close and label. Preserve the filtrate in a manner consistent with the chemical analyses to be performed.

APPENDIX F

ATOMIC ABSORPTION SPECTROMETRIC PROCEDURES FOR Hg, Sb, AND As

APPENDIX F
ATOMIC ABSORPTION SPECTROMETRIC PROCEDURES
FOR Hg, Sb, AND As

F.1 MERCURY ANALYSIS

F.1.1 Scope and Application

The cold vapor mercury analysis described here is applicable for Level 1 determination of Hg in hydrogen peroxide and ammonium persulfate impinger solutions, bulk liquids, dilute HNO_3 solutions resulting from the Parr bomb combustion of fuels and XAD-2 resin samples, and aqua regia solutions from the digestion of particulates. Sensitivity and detection limits are 0.004 and 0.001 µg, respectively, with an upper limit of 0.25 µg.

F.1.2 Summary of Method

The cold vapor mercury analysis is based on the reduction of mercury species in acid solution with stannous chloride and the subsequent sparging of elemental mercury, with nitrogen, through a quartz cell where its absorption at 253.7 nm is monitored.

F.1.3 Apparatus

- Mercury reduction apparatus--The usual design, consisting of a jar incorporating a two-hole rubber stopper through which a gas bubbler tube and a short gas outlet tube pass, can be used. A U tube with a glass frit on one side has been found to be satisfactory. The frit serves as a mixing device as well as the gas bubbler, thus eliminating the need for a separate magnetic stirrer and a stirring bar to mix the reductor contents.

- Atomic absorption spectrophotometer--Use a mercury hollow cathode lamp at a wavelength of 253.7 nm (or equivalent).

- Absorption cell--A cylindrical tube approximately 25 mm I.D. × 125 mm long, with quartz windows, and incorporating inlet and outlet side arms to permit introduction and discharge of carrier gas. This type of cell is available commercially from several manufacturers of atomic absorption equipment, or it may be constructed from readily available materials. In the latter case, the cell should be tested carefully for possible leakage after assembly. The cell is mounted in the optical path of the AAS.

- Flowmeter--Capable of measuring a gas flow on the order of 1.9 L/min (4 ft^3/h).
- Scavenging tube--This tube is filled with soda lime and is connected between the gas outlet tube of the reduction vessel and the inlet side arm of the absorption cell with Tygon tubing. The soda lime is replaced every 25 determinations; otherwise a loss in sensitivity occurs.
- Erlenmeyer flasks--125 mL.
- Beakers--150 mL.
- Pellet press.
- Funnels.
- Filter paper--Whatman #41.

F.1.4 Reagents

- Stock mercury solution, approximately 1 g/L (1,000 ppm)--Weigh 1 g of pure, elemental mercury to the nearest 0.1 mg and dissolve in a solution consisting of 150 mL deionized water and 50 mL concentrated HNO_3 (specific gravity of 1.42). Dilute this solution to 1,000 mL with deionized water. The final solution contains approximately 1,000 ppm mercury (record exact concentration) in a matrix of 5 percent (v/v) nitric acid. A commercially obtained 1,000 ppm Hg solution can also be used.
- Standard mercury solutions--Prepare working standard solutions of mercury down to 1 ppm by serial dilutions of the 1,000 ppm Hg stock solution with 5 percent (v/v) HNO_3. Such solutions can be assumed to be stable for up to one week. Below 1 ppm Hg, standard solutions should be prepared daily and diluted with 5 percent (v/v) HNO_3 and/or deionized water as appropriate so the final solution matrix is approximately 1 percent (v/v) HNO_3.
- 1:1 Nitric acid solution--Dilute 500 mL concentrated nitric acid to 1,000 mL.
- Stannous chloride solution--Dissolve 20 g of $SnCl_2 \cdot H_2O$ in 20 mL concentrated HCl (warm the solution to accelerate the dissolution process) and dilute to 100 mL.
- Potassium permanganate solution--Dissolve 5.0 g $KMnO_4$ in deionized water and dilute to 1 L.

- Nitrogen carrier gas.
- Nitric acid, concentrated.
- Hydrochloric acid, concentrated.
- Benzoic acid.

F.1.5 Procedure

F.1.5.1 Standardization--

Standards in the range of 1-10 ppb are made. To the reduction vessel, transfer 10 mL 1:1 nitric acid solution, 3 mL concentrated H_2SO_4, 5 mL of a standard solution, and deionized water to bring the volume to a total of 50 mL. Add 5 mL of stannous chloride solution. Close the system and immediately initiate the nitrogen flow. The optimum flow rate will vary from system to system; therefore, several flow rates should be tried until maximum sensitivity is obtained. Repeat the procedure for varying concentrations of mercury throughout the specified range. The glass frit is cleansed between analyses by flushing with 1:1 nitric acid followed by deionized water. Blanks should be run using deionized water. Plot absorption (peak height) against standard concentration to obtain a calibration curve.

F.1.5.2 Analysis--

In the determination of mercury by the cold vapor technique, certain volatile organic materials may absorb at 253.7 nm. If this is expected, the sample should be analyzed by the regular procedure and again under oxidizing conditions, i.e., without the addition of stannous chloride. The true mercury concentration can be obtained by taking the difference of the two values.

- Aqueous samples are analyzed by the same procedure as that used for standardization. If a larger sample size is used resulting in a total volume greater than 50 mL, a new calibration curve must be constructed using the new total volume.

- 30 percent H_2O_2 has shown an interference by consuming the stannous chloride reducing agent. This problem is circumvented by decomposing the excess H_2O_2 with permanganate prior to stannous chloride addition. Pipet an aliquot into a 125-mL Erlenmeyer and add 10 mL concentrated HNO_3. Add $KMnO_4$ solution, stirring until the MnO_2 precipitate that forms will not redissolve. At this point add 2 mL concentrated H_2SO_4 and 1 drop 30 percent H_2O_2.

After precipitate has redissolved, continue adding $KMnO_4$ dropwise until a permanent reddish color is obtained. Transfer contents to reduction apparatus and adjust volume to approximately 50 mL. Proceed as per the standardization procedure.

- The presence of the silver nitrate catalyst in the ammonium persulfate solution has been shown to yield low Hg recoveries. Removal of Ag^+ by addition of Cl^- followed by filtration has been found to be an effective procedure for the removal of this interference. Pipet an aliquot into a 150-mL beaker. Add 10 mL concentrated HNO_3 and 2 mL HCl. Filter through #41 Whatman filter. Wash several times with deionized water and dilute filtrate to approximately 50 mL. Transfer filtrate to reduction vessel and proceed as per standardization procedure.

- In analyzing organic solids, aliquots from Parr bomb decomposition over acid are used. If there is doubt as to whether the sample has undergone complete oxidation during combustion, add 5 percent potassium permanganate solution dropwise until a pink color persists. Proceed with the determination as described under standardization. As the bomb ages, there may be a tendency for mercury to become trapped in the bomb wall fissures during combustion. In addition, if the same bomb is used for normal calorimetry work, there may be a tendency for mercury to accumulate in the bomb with time. Consequently, before a series of mercury determinations is undertaken, several blank determinations should be made by firing benzoic acid pellets (approximately 1 g) in place of the sample. Benzoic acid firings should be repeated until a stable, consistently low blank value is obtained. This final blank value is then used to correct the mercury values obtained for subsequent samples. The condition of the interior of the bomb should be inspected at frequent intervals. If evidence of significant pitting or corrosion is observed (usually indicated by erratic mercury values for samples or benzoic acid blanks), the bomb should be returned to the manufacturer for reconditioning.

- To analyze particulates, aliquots from the aqua regia digestion are used. Proceed with the determination as described under standardization.

F.1.6 Precision and Accuracy

Mercury at a concentration of 0.4 µg/L yields a precision of ±21.2 percent RSD with a relative error of 2.4 percent.

F.2 ANTIMONY ANALYSIS

F.2.1 Scope and Application

This method is applicable for the determination of antimony in the ammonium persulfate solutions obtained from SASS train impingers.

F.2.2 Summary of Method

Organic antimony-containing compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the sample to fumes of sulfur trioxide. The antimony liberated, together with the inorganic antimony originally present, is subsequently reacted with potassium iodide and stannous chloride, and finally with sodium borohydride to form stibine. The stibine is removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame in an atomic absorption spectrometer. The gas sample absorption is measured at 217.6 nm. Since the stibine is freed from the original sample matrix, interferences in the flame are minimized.

F.2.3 Apparatus

- Stibine vapor generator--(Figure F-1) consists of: (1) a 100-mL capacity three-neck round-bottom flask; (2) gas dispersion tube, coarse frit (Scientific Glass Apparatus Co. No. JG-8500 has been found satisfactory); and (3) 2-mL capacity medicine dropper, or 5-mL capacity automatic pipetter.

- Atomic absorption spectrophotometer--Use an antimony hollow cathode lamp at a wavelength of 217.6 nm. A three-slot burner or equivalent is to be used. The fuel is hydrogen (hydrogen diffusion flame) and nitrogen is used as the stibine carrier.

F.2.4 Reagents

- Antimony standard solution I, 1.00 mL = 100 μg Sb--Dissolve 274.3 mg antimony potassium tartrate, $(SbO)KC_4H_4O_6 \cdot 1/2H_2O$, in deionized water and dilute to 1 L with deionized water.

- Antimony standard solution II, 1.00 mL = 10 μg Sb--Dilute 50.0 mL antimony solution I to 500.0 mL with deionized water.

- Antimony standard solution III, 1.0 mL = 0.10 μg Sb--Dilute 5.0 mL antimony standard solution II to 500.0 mL with deionized water. Prepare fresh before each use.

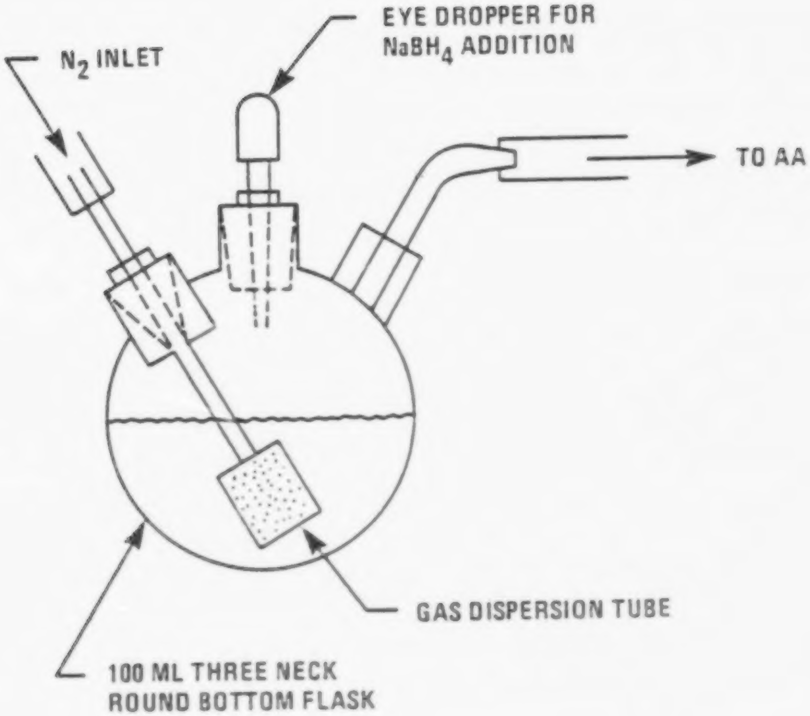
EYE DROPPER FOR
$NaBH_4$ ADDITION
N_2 INLET
TO AA
GAS DISPERSION TUBE
100 ML THREE NECK
ROUND BOTTOM FLASK

Figure F-1. Hydride evolution apparatus.

- Hydrochloric acid, concentrated (specific gravity 1.19)
- Nitric acid, concentrated (specific gravity 1.41).
- Potassium iodide solution, 15 g/100 mL--Dissolve 15 g KI in 100 mL deionized water. This solution is stable when stored in an amber bottle.
- Sodium borohydride solution, 4 g/100 mL--Dissolve 4 g $NaBH_4$ pellets in 100 mL deionized water (Alfa Products No. 14122 has been found satisfactory). Prepare fresh just before each use.
- Stannous chloride solution, 4.6 g/100 mL concentrated HCl--Dissolve 5 g $SnCl_2 \cdot H_2O$ in 100 mL concentrated HCl (specific gravity 1.19). This solution is stable if a few pieces of mossy tin are added to prevent oxidation.
- Sulfuric acid 9M--Cautiously, and with constant stirring and cooling, add 250 mL concentrated H_2SO_4 (specific gravity 1.84) to 250 mL deionized water.

F.2.5 Procedure

1. Prepare, in 150-mL beakers, a blank and sufficient standards containing from 0.0 to 1.5 µg Sb by diluting 0.0 to 15.0 mL portions of antimony standard solution III to 100 mL with deionized water. Place 25-mL aliquots of the impinger solution into beakers and add water as with the blank and standards.
2. To each beaker add 7 mL 9M H_2SO_4 and 5 mL concentrated HNO_3. Add a small boiling chip and carefully evaporate to fumes of SO_3. Maintain an excess of HNO_3 until all organic matter is destroyed as evidenced by a clear solution. This prevents darkening of the solution and possible reduction and loss of antimony. Cool, add 25 mL deionized water, and again evaporate to fumes of SO_3 to expel oxides of nitrogen.
3. Cool, and adjust the volume of each beaker to approximately 50 mL with deionized water.
4. To each beaker, add successively, with thorough mixing after each addition, 4 mL concentrated HCl, 1 mL KI solution, and 0.5 mL $SnCl_2$ solution. Allow about 15 min for reaction.
5. To set the N_2 carrier gas flow rate, place 55 mL of deionized water in the round-bottomed flask and put a rubber stopper in place of the medicine dropper. Increase the N_2 flow slowly until a maximum is reached that still avoids carrying liquid into the tubing leading to the AA instrument. Empty the flask and begin analyzing the samples by transferring the contents of each beaker, one at a time, to the flask and proceeding with the $NaBH_4$ reaction.

6. Fill the medicine dropper with ~1 mL $NaBH_4$ solution and insert into a one-hole rubber stopper that has been tightly fitted into the center neck of the three-neck round-bottom flask. Press the dropper and rubber stopper both in tightly.

7. Quickly add the $NaBH_4$ solution all at once to the sample solution. After the absorbance has reached a maximum and has returned to the baseline as measured by the AAS instrument, remove the flask. Rinse the gas dispersion tube in deionized water before proceeding to the next sample. Treat each succeeding sample, blank, and standard in a like manner.

F.3 ARSENIC ANALYSIS

F.3.1 Scope and Application

Arsenic analysis by hydride generation and atomic absorption spectrometric detection is applicable for the analysis of ammonium persulfate solutions obtained from SASS train impingers. Detection limit for the procedure is 0.1 μg with a calculated sensitivity of 0.8 μg. Either of two arsine evolution methods can be used: gas can be generated in a reaction with stannous chloride and zinc slurry, or in a reaction with sodium borohydride. Some interferences have been reported for this arsenic procedure. In particular, it has been found that excess HNO_3 must be removed prior to the addition of either the Zn slurry or $NaBH_4$.

F.3.2 Summary of Method

The procedure entails the reduction and conversion of arsenic to its hydride in acid solution with either $SnCl_2$ and metallic Zn or $NaBH_4$. The volatile hydride is swept from the reaction vessel, in a stream of argon, into an argon-hydrogen flame in an atomic absorption spectrophotometer. There the hydride is decomposed and its concentration monitored at the resonance wavelength 193.7 nm.

F.3.3 Apparatus

- Arsine vapor generator--The apparatus used for the generation of stibine may be used here. Connect the outlet of the reaction vessel to the auxiliary oxidant input of the spectrophotometer burner with Tygon tubing and connect the inlet of the reaction vessel to the outlet side of the auxiliary oxidant control valve of the instrument.

- Atomic absorption spectrophotometer--Use an arsenic hollow cathode lamp at a wavelength of 193.7 nm. A Boling burner head is to be used; the flame source is argon-hydrogen (about 8 L/min each). Argon (~ 1 L/min), connected as the auxiliary oxidant, serves to carry the arsine into the flame.

F.3.4 Reagents

- Potassium iodide solution--Dissolve 20 g KI in 100 mL deionized water.

- Stannous chloride solution--Dissolve 100 g $SnCl_2$ in 100 mL concentrated HCl.

- Zinc slurry--Add 50 g zinc metal dust (200 mesh) to 100 mL deionized water.

- Diluent--Add 100 mL 18 N H_2SO_4 and 400 mL concentrated HCl to 400 mL deionized water in a 1-L volumetric flask and bring to volume with deionized water.

- Sodium borohydride solution--Dissolve 5 g $NaBH_4 \cdot H_2O$ in 100 mL deionized water. Make fresh prior to each use.

- Arsenic solutions--

  1. Stock arsenic solution--Dissolve 1.3209 g arsenic trioxide, As_2O_3, in 100 mL deionized water containing 4 g NaOH and dilute to 1,000 mL with deionized water. 1.00 mL solution contains 1.00 mg As.

  2. Intermediate arsenic solution--Pipet 1 mL stock arsenic solution into a 100-mL volumetric flask and bring to volume with deionized water containing 1.5 mL concentrated HNO_3/L. 1.00 mL solution contains 10 μg As.

  3. Standard arsenic solution--Pipet 10 mL intermediate arsenic solution into a 100-mL volumetric flask and bring to volume with deionized water containing 1.5 mL concentrated HNO_3/L. 1.00 mL solution contains 1 μg As.

F.3.5 Procedures

F.3.5.1 Sample Preparation--Ammonium Persulfate Samples--

To a 25-mL aliquot in a 150-mL beaker, add 5 mL concentrated HNO_3 and 6 mL 18 N H_2SO_4. Evaporate to SO_3 fumes. To avoid the loss of arsenic, maintain oxidizing conditions at all times by adding small amounts of nitric acid whenever the red brown NO_2 fumes disappear. Cool, transfer to a 50-mL volumetric, add 20 mL concentrated HCl, and dilute to volume.

F.3.5.2 Preparation of Standards--

Transfer 0.5, 1.0, 1.5, and 2.0 mL of standard arsenic solution to 100-mL volumetric flasks and bring to volume with diluent to obtain concentrations of 5, 10, 15, and 20 μg/L arsenic.

F.3.5.3 Treatment of Samples and Standards--

Transfer a 25-mL portion of prepared sample or standard to the reaction vessel and add 1 mL potassium iodide solution. If the Zn slurry addition method is to be followed, add 0.5 mL $SnCl_2$ solution. Allow at least 10 min for the metal to be reduced to its lowest oxidation state. Initiate the argon flow. Fill the medicine dropper either with 1.50 mL zinc slurry that has been kept in suspension with the magnetic stirrer, or with 1.50 mL $NaBH_4$ solution. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce either the zinc slurry or the $NaBH_4$ solution into the sample or standard. The metal hydride will produce a peak almost immediately. When the recorder pen returns to the baseline, remove the reaction vessel, empty, and proceed with the next sample.

Please note that if Zn is used, a 10-cm long polyethylene tube filled with glass wool should be connected to the generator exit tube in order to keep particulate matter out of the burner.

F.3.6 Precision and Accuracy

Replicate 10-μg/L samples exhibit a relative standard deviation of ±6.0 percent and a relative error of ±1.0 percent.